

On the standard potentials of mercury, and the equilibrium $\text{Hg}^{2+} + \text{Hg(l)} \rightleftharpoons \text{Hg}_2^{2+}$ in nitrate and perchlorate solutions

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With 10 figures in the text

The equilibrium



may be studied either by determining the *total* concentrations c_1 and c_2 in an equilibrium mixture by chemical analysis, or by combining emf data for the half-cells $\text{Hg}_2^{2+}/\text{Hg}$ and Hg^{2+} , $\text{Hg}_2^{2+}/\text{Pt}$. Since the equilibrium constant is of the order of 100, and it is not easy to determine the small amount of mercury (II) in the presence of large amounts of mercury (I) by chemical means, the emf method is far more accurate.

If the formal (molar) electrode potentials of $\text{Hg}_2^{2+}/\text{Hg}$ and Hg^{2+} , $\text{Hg}_2^{2+}/\text{Pt}$ are e_{10}^* and e_{21}^* for a certain ionic medium, then at 25° C

$$e_{21}^* - e_{10}^* = 59.16 \log K \quad (2)$$

The formal (stoichiometric) potentials e^* , and the equilibrium "constant" K , can be expected to vary with the ionic medium used. This variation may, more or less formally, be ascribed to Coulomb-force activity factors f_i and to the formation of complexes between mercury and the ions of the medium. In addition, the hydrated mercury (II) ion is an acid of considerable strength: according to Hietanen and Sillén [1], the $\text{p}K_a$ values are 3.7 and 2.6 at 25° C in a 0.5 M NaClO_4 medium. Thus OH complexes are readily formed with mercury (II), whereas the acidity of mercury (I) seems to be much weaker [5] and will be neglected in the following.

The standard value K^0 of K , and the standard electrode potentials e^0 , should be valid for hydrated but otherwise uncomplexed Hg_2^{2+} and Hg^{2+} ions at infinite dilution. They are related by

$$e_{21}^0 - e_{10}^0 = 59.16 \log K^0 \quad (2a)$$

To find e_{21}^0 , e_{10}^0 , and K^0 from measured values of e_{21}^* , e_{10}^* , and K , one may in principle first correct c_2 for OH complexes, using known values of the K_a , and then correct for complexes with the ions of the medium and for activity factors

by extrapolating to infinitely dilute solution. Such an extrapolation meets with difficulties because of the strong acidity of Hg^{2+} .

Infeldt and Sillén [2] studied the variation of e_{21}^* and e_{10}^* with nitrate ion concentration in nitrate-perchlorate mixtures of total anion concentration 0.5 M or 3.0 M. Their data indicated that both mercury (I) and mercury (II) form stronger complexes with nitrate than with perchlorate. Complexity constants for $\text{Hg}^{2+}\text{-NO}_3^-$ and $\text{Hg}_2^{2+}\text{-NO}_3^-$ were calculated on the usual formal assumption that ClO_4^- forms no complexes.

Abel [3] determined the equilibrium constant, K , as 119.8 in about 0.3 M HNO_3 at 25°C , by direct analysis. Jonsson, Qvarfort, and Sillén [4] found $K = 129.2 \pm 1.0$ at 25°C from measurements of e_{21}^* and e_{10}^* in an ionic medium of 0.49 M $\text{NaClO}_4 + 0.01\text{ M HClO}_4$. When these two values were corrected for hydrolysis and for nitrate complex formation, the values 130 and 132.4 were found for $[\text{Hg}_2^{2+}]/[\text{Hg}^{2+}]$ (Forsling, Hietanen, and Sillén [5]). Because of this good agreement it seemed reasonable to assume that the activity factors of the two bipoisitive ions Hg^{2+} and Hg_2^{2+} approximately cancelled each other out. It was then assumed that the standard equilibrium constant K^0 was 130 ± 10 , and this value was used in deducing the standard potentials of mercury [5]. We now know that this agreement was spurious (p. 121).

Recently, Schwarzenbach and Anderegg [6] studied cells containing nitrate solutions, at concentrations from 0.013 to 1.00 M, and temperatures from 0°C to 40°C , but always with a hydrogen ion concentration of 0.01 M. By extrapolation to infinite dilution, and interpolation between the temperatures (they have no measured data for exactly 25°C) they found $K^0 = 83.4$ at 25°C . The two values [5, 6] for K^0 , 130 and 83.4, would give $59.16 \log K^0 = 125$ and 113.7 mV. However, a difference of more than 11 mV in the emf is much more than one would expect from experimental error.

At first, a number of the experiments of both the Zürich and Stockholm groups were repeated, as Schwarzenbach and Anderegg [6] had suggested that the discrepancies might be due to the fact that the Stockholm workers had not waited sufficiently long for equilibrium. Our new experiments confirmed the previous Stockholm data, which had moreover been obtained independently by several workers. We could also quickly remove all suspicions we might have had about gross errors in Schwarzenbach's and Anderegg's data. Sometimes we found values that deviated by 1 mV or so from theirs, but certainly no differences of the order of 11 mV were detected.

Since the data of both groups were correct, something in our initial assumptions must have been incorrect. An extended series of emf measurements has now led us to the somewhat unexpected conclusion that mercury (I) may form stronger complexes with the perchlorate ion than does mercury (II).

Composition of solutions

Parallel experiments were always carried out with NO_3^- and ClO_4^- in the ionic medium. We shall write

$$x = [\text{X}^-]; \quad \text{X}^- = \text{NO}_3^- \text{ or } \text{ClO}_4^- \quad (3)$$

Each solution contained H^+ (h M) and one or two of the ions Ag^+ , Hg_2^{2+} , and Hg^{2+} , the total (analytical) concentrations of which will be denoted by c_a , c_1 , and c_2 . The balance was Na^+ . Thus, in the solutions denoted by (x) , (c_a, x) , (c_1, x) and (c_1, c_2, x) , the molar concentrations were

	H^+	Ag^+	Hg_2^{2+}	Hg^{2+}	Na^+	X^-
x	h	—	—	—	$(x-h)$	x
c_a, x	h	c_a	—	—	$(x-h-c_a)$	x
c_1, x	h	—	c_1	—	$(x-h-2c_1)$	x
c_1, c_2, x	h	—	c_1	c_2	$(x-h-2c_1-2c_2)$	x

Usually, c_a , c_1 , and c_2 were chosen to be much smaller than x . In all our experiments $h=0.010$ M, since this was the acidity used by Jonsson, Qvarfort, and Sillén [4], and by Schwarzenbach and Anderegg [6].

Types of cell

The following types of cell were used:

$$\left. \begin{array}{l} \text{cell A } (x', x'') = Ag/c_a, x'/c_a, x''/Ag \\ \text{cell B } (x', x'') = Ag/c_a, x'/c_1, x''/Hg \\ \text{cell C } (x', x'') = Ag/c_a, x'/c_1, c_2, x''/Pt \end{array} \right\} \quad (5)$$

In some series of experiments, x' was kept constant = 1 M, whereas x'' was varied continuously by titration. In other series, we kept $x' = x'' = x$ ("fixed cells").

Tentative expressions for the emf

Liquid-junction potentials.—In the following discussion, we shall consider the emf E of each cell as made up of the difference between the electrode potentials of the "plus" (right) and "minus" (left) half-cells, plus the liquid-junction potential E_j .

$$E = e_+(x'') - e_-(x') + E_j(x'/x'') \quad (6)$$

We shall moreover make the tentative assumption—which is confirmed by our experimental results—that E_j can be regarded as the difference between two quantities $e_j(x)$, each of which is a function only of the x in the solution:

$$E_j(x'/x'') = e_j(x'') - e_j(x') \quad (7)$$

If this is so, E can be regarded as the difference between two terms, each of which depends only on the solution at one of the electrodes:

$$E = (e_+(x'') + e_j(x'')) - (e_-(x') + e_j(x')) \quad (8)$$

The function $e_j(x)$ contains an arbitrary constant, which will however cancel out in (7) and (8). We shall choose it so as to make

$$e_j(0) = 0 \quad (7 \text{ a})$$

Our assumption (7) may be justified by the following argument. The concentrations of Ag^+ , Hg_2^{2+} , and Hg^{2+} are in general small compared with Na^+ , and the equivalent conductances (61.9 for Ag^+ , and ≈ 55 for the bipoisitive ions [10]) do not differ very much from that of Na^+ (50.1). Thus $E_j(x'/x'')$ will be approximately equal to E_j at the junction

$$h \text{ M H}^+, (x' - h) \text{ M Na}^+, x' \text{ M X}^- / h \text{ M H}^+, (x'' - h) \text{ M Na}^+, x'' \text{ M X}^-$$

Provided one of the assumptions used in deriving the Henderson equation is fulfilled, namely that the solution in any part of the diffusion layer can be regarded as a mixture of the two terminal solutions, then for any intermediate solution, with $x = x_1$, E_j may be divided into two parts:

$$E_j(x'/x'') = E_j(x'/x_1) + E_j(x_1/x'') \quad (9)$$

However, if (9) is true for any set of values for x' , x_1 , and x'' , then (7) must be generally valid.

Formal potentials and formal emfs.—The electrode potentials referred, as usual, to the standard hydrogen electrode may be expressed either by means of the three formal potentials e^* , which vary with x (and with the acidity), or by means of the constant standard potentials e^0 :

$$e(c_a, x/\text{Ag}) = e_a^*(x) + 59.16 \log c_a = e_a^0 + 59.16 \log \{\text{Ag}^+\} \quad (10 \text{ a})$$

$$e(c_1, x/\text{Hg}) = e_{10}^*(x) + 29.58 \log c_1 = e_{10}^0 + 29.58 \log \{\text{Hg}_2^{2+}\} \quad (10 \text{ b})$$

$$\begin{aligned} e(c_1, c_2, x/\text{Pt}) &= e_{21}^*(x) + 59.16 \log c_2 - 29.58 \log c_1 \\ &= e_{21}^0 + 59.16 \log \{\text{Hg}_2^{2+}\} - 29.58 \log \{\text{Hg}_2^{2+}\} \end{aligned} \quad (10 \text{ c})$$

For the discussion of the experimental data it is convenient to eliminate the concentration terms with c_a , c_1 , and c_2 by calculating the *formal emfs* E^* :

$$E_A^*(x', x'') = E_A(x', x'') \quad (11 \text{ a})$$

$$E_B^*(x', x'') = E_B(x', x'') - 29.58 \log c_1 + 59.16 \log c_a \quad (11 \text{ b})$$

$$E_C^*(x', x'') = E_C(x', x'') + 29.58 \log c_1 - 59.16 \log c_2 + 59.16 \log c_a \quad (11 \text{ c})$$

From (11), (8), and (10) we find

$$E_A^*(x', x'') = e_a^*(x'') + e_j(x'') - (e_a^*(x') + e_j(x')) \quad (12 \text{ a})$$

$$E_B^*(x', x'') = e_{10}^*(x'') + e_j(x'') - (e_a^*(x') + e_j(x')) \quad (12 \text{ b})$$

$$E_C^*(x', x'') = e_{21}^*(x'') + e_j(x'') - (e_a^*(x') + e_j(x')) \quad (12 \text{ c})$$

Total concentration and activity.—It follows from (10) that the differences between e^* and e^0 depend on the ratios between the total concentrations and the activities of the hydrated uncomplexed ions, thus $c_a \{Ag^+\}^{-1}$ etc. We shall first introduce the Coulomb-force molar activity factors $f_i(x)$ of the hydrated uncomplexed ions:

$$\{Ag^+\} = f_a [Ag^+]; \{Hg_2^{2+}\} = f_1 [Hg_2^{2+}]; \{Hg^{2+}\} = f_2 [Hg^{2+}] \quad (13)$$

Moreover, the ions may form complexes with the ions of the medium, and Hg^{2+} also with OH^- , so that the total concentrations will be

$$\begin{aligned} c_a &= [Ag^+] + [AgX] + [AgX_2] + \dots = [Ag^+] (1 + \beta_{1,a} x + \beta_{2,a} x^2 + \dots) \\ &= [Ag^+] (1 + \sum \beta_{n,a} x^n) \end{aligned} \quad (14 a)$$

$$c_1 = [Hg_2^{2+}] + [Hg_2X^+] + [Hg_2X_2] + \dots = [Hg_2^{2+}] (1 + \sum \beta_{n,1} x^n) \quad (14 b)$$

$$\begin{aligned} c_2 &= [Hg^{2+}] + [HgX^+] + [HgX_2] + \dots + [HgOH^+] + [HgOHX] + [HgOHX_2] + \dots + \\ &\quad + [Hg(OH)_2] + [Hg(OH)_2X^-] + \dots \\ &= [Hg^{2+}] (1 + \sum \beta_{n,2} x^n) (1 + K_{a1} h^{-1} + K_{a2} K_{a1} h^{-2}) \end{aligned} \quad (14 c)$$

In (14), the β_n are the complexity products for the cations and X^- , K_{a1} and K_{a2} are the apparent acidity constants of $Hg(II)$ in the ionic medium with $[X^-] = x$. Both the K_a and the β are functions of x . In the equations, x should be the free concentration of X^- , whereas in our experimental part the total concentration is used. The fraction of X^- bound by complexing is of the order of $c\beta_1$; it would give, for instance, a difference between data with different values of c_1 . The subsequent data will show that for NO_3^- , β_1 is of the order of $1-2 M^{-1}$ whereas the c are 0.001 to 0.010. The correction will then be within the error of extrapolation.

Applying (10), (13), and (14) we find

$$e_a^*(x) = e_a^0 + 59.16 \log f_a - 59.16 \log (1 + \sum \beta_{n,a} x^n) \quad (15 a)$$

$$e_{10}^*(x) = e_{10}^0 + 29.58 \log f_1 - 29.58 \log (1 + \sum \beta_{n,1} x^n) \quad (15 b)$$

$$\begin{aligned} e_{21}^*(x) &= e_{21}^0 + 59.16 \log f_2 - 59.16 \log (1 + \sum \beta_{n,2} x^n) - \\ &\quad - 59.16 \log (1 + K_{a1} h^{-1} + K_{a1} K_{a2} h^{-2}) - 29.58 \log f_1 + \\ &\quad + 29.58 \log (1 + \sum \beta_{n,1} x^n) \end{aligned} \quad (15 c)$$

The deviation functions.—It will be convenient to introduce deviation functions $D_a(x)$ etc., which also include the variation of the liquid junction potential, since the latter cannot be distinguished sharply from the other terms:

$$D_a(x) = 59.16 \log f_a(x) - 59.16 \log (1 + \sum \beta_{n,a}(x) x^n) + e_j(x) \quad (16 a)$$

$$D_1(x) = 29.58 \log f_1(x) - 29.58 \log (1 + \sum \beta_{n,1}(x) x^n) + e_j(x) \quad (16 b)$$

$$D_2(x) = 29.58 \log f_2(x) - 29.58 \log (1 + \sum \beta_{n,2}(x) x^n) + D_{2h}(x) + e_j(x) \quad (16 c)$$

In (16 c)

$$D_{2h}(x) = 29.58 \log (1 + K_{a1}^0 h^{-1} + K_{a1}^0 K_{a2}^0 h^{-2}) - 29.58 \log (1 + K_{a1}(x) h^{-1} + K_{a1}(x) K_{a2}(x) h^{-2}) \quad (16 d)$$

and K_{a1}^0 , K_{a2}^0 are the acidity constants of Hg^{2+} at infinite dilution.

When $x \rightarrow 0$, all these $D(x)$ functions will tend to zero, since then $f_1 \rightarrow 1$, $e_j \rightarrow 0$ (7 a), $K_{a1} \rightarrow K_{a1}^0$, and $K_{a2} \rightarrow K_{a2}^0$:

$$D_a(0) = D_1(0) = D_2(0) = 0 \quad (16 e)$$

We shall introduce the symbol $e_{21}^{0'}$ for e_{21}^0 uncorrected for the hydrolysis of Hg^{2+} :

$$e_{21}^{0'} = e_{21}^0 - 59.16 \log (1 + K_{a1}^0 h^{-1} + K_{a1}^0 K_{a2}^0 h^{-2}) \quad (17)$$

From (15), (16), and (17)

$$e_a^*(x) = e_a^0 + D_a(x) - e_j(x) \quad (18 a)$$

$$e_{10}^*(x) = e_{10}^0 + D_1(x) - e_j(x) \quad (18 b)$$

$$e_{21}^*(x) = e_{21}^{0'} + 2 D_2(x) - D_1(x) - e_j(x) \quad (18 c)$$

From (12) and (18) we find the following relationships between the experimentally determined E^* , the deviation functions D , and the standard electrode potentials e^0 :

$$E_A^*(x', x'') = D_a(x'') - D_a(x') \quad (19 a)$$

$$E_B^*(x', x'') = e_{10}^0 - e_a^0 + D_1(x'') - D_a(x') \quad (19 b)$$

$$E_C^*(x', x'') = e_{21}^{0'} - e_a^0 + 2 D_2(x'') - D_1(x'') - D_a(x') \quad (19 c)$$

By means of the equations (19), we shall now proceed to give formulas for determining the $D(x)$ and the e^0 . In (16) each deviation function is divided into one term for the Coulomb-force activity factor, one for complex formation with the medium, and one for the liquid junction potentials. In calculating the $D(x)$ it is irrelevant whether it is possible to make such a division strictly.

Calculations of $D(x)$, e^0 and K

The deviation functions D can each be obtained, using (19), by two or three different combinations of our experimental data, which allows a check:

$$D_a(x) - D_a(1) = E_A^*(1, x) \quad (20 a)$$

$$= E_B^*(1, x) - E_B^*(x, x) \quad (20 b)$$

$$= E_C^*(1, x) - E_C^*(x, x) \quad (20\ c)$$

$$D_1(x) - D_1(1) = E_B^*(x, x) - E_B^*(1, 1) + E_A^*(1, x) \quad (21\ a)$$

$$= E_B^*(1, x) - E_B^*(1, 1) \quad (21\ b)$$

$$D_2(x) - D_2(1) = \frac{1}{2} [E_B^*(x, x) - E_B^*(1, 1) + E_C^*(x, x) - E_C^*(1, 1)] + E_A^*(1, x) \quad (22\ a)$$

$$= \frac{1}{2} [E_B^*(1, x) - E_B^*(1, 1) + E_C^*(1, x) - E_C^*(1, 1)] \quad (22\ b)$$

All the $D(x)$ are thus for convenience referred to the value for $x=1$, since the extrapolation to infinite dilution is not too certain.

The standard potentials.—By suitable combinations of E^* we may find from (19) expressions which would give a difference between two e^0 values plus a number of D terms which vanish (16 e) as x tends to zero:

$$e_{10}^0 - e_a^0 + D_1(x) - D_a(x) = E_B^*(1, x) - E_A^*(1, x) \quad (23\ a)$$

$$= E_B^*(x, x) \quad (23\ b)$$

$$e_{21}^{0'} - e_a^0 + 2 D_2(x) - D_1(x) - D_a(x) = E_C^*(1, x) - E_A^*(1, x) \quad (24\ a)$$

$$= E_C^*(x, x) \quad (24\ b)$$

$$\frac{1}{2} (e_{10}^0 + e_{21}^{0'}) - e_a^0 + D_2(x) - D_a(x) = \frac{1}{2} [E_B^*(1, x) + E_C^*(1, x)] - E_A^*(1, x) \quad (25\ a)$$

$$= \frac{1}{2} [E_B^*(x, x) + E_C^*(x, x)] \quad (25\ b)$$

The apparent *equilibrium constant* (1), $K(x) = c_2/c_1$, and $e_{21}^{0'} - e_{10}^0$ are found from (26), which is derived from (2), (12), and (19).

$$59.16 \log K(x) = e_{21}^*(x) - e_{10}^*(x) = e_{21}^{0'} - e_{10}^0 + 2 D_2(x) - 2 D_1(x) = \quad (26)$$

$$= E_C^*(1, x) - E_B^*(1, x) \quad (26\ a)$$

$$= E_C^*(x, x) - E_B^*(x, x) \quad (26\ b)$$

From (26), (2 a), (16 b-d), and (17), or from (13), (14 b), and (14 c)

$$\frac{K(x)}{K^0} = \frac{f_2(1 + \sum \beta_{n,1} x^n)}{f_1(1 + \sum \beta_{n,2} x^n)} \cdot (1 + K_{a1} h^{-1} + K_{a1} K_{a2} h^{-2})^{-1} \quad (26\ c)$$

Experimental

Reagents and apparatus

Mercury (II) perchlorate and nitrate solutions were prepared by dissolving weighed amounts of HgO (Merck p.a.) in a known excess of HNO₃ or HClO₄. As a check, the Hg²⁺ concentration was determined by titration with SCN⁻, using Fe³⁺ as an indicator.

Mercury (I) perchlorate and nitrate solutions were prepared by shaking excess of metallic mercury, usually for a couple of days, with mercury (II) perchlorate or nitrate solution. The total mercury content ($2c_1 + c_2$) was determined by electrolysis, after which the solution was always tested for absence of mercury. The small amount of mercury (II), c_2 , which did not necessarily correspond to equilibrium with Hg(l) , was determined by measuring the redox potential before and after adding a known amount of Hg^{2+} , as described by Jonsson, Qvarfort and Sillén [4].

Silver perchlorate solutions were prepared and analysed as described by Hietanen [7]. Silver nitrate (Kebo p.a.) was weighed in; the concentration was checked by ion exchanger analysis (giving NO_3^-) and Volhard titration, standardizing against metallic silver.

Sodium perchlorate was prepared by mixing HClO_4 and NaHCO_3 solutions, and analysed as described by Hietanen [7]. The sodium nitrate was Merck p.a.

The perchloric and nitric acids were Kebo p.a.

The concentrations of ClO_4^- and NO_3^- in the various stock solutions were determined with an ion exchange method [7].

The glass cell was of the type described by Forsling, Hietanen, and Sillén [5]; this type is usually referred to as a "Wilhelm" apparatus in this institution.

The *platinum* electrodes were bright Pt foils which were cleaned with half-concentrated HNO_3 and ignited in an alcohol flame before using. As *silver* electrodes, Ag, AgCl electrodes according to Brown were used as in the work of Biedermann and Sillén [8]. The *mercury* electrode was a mercury pool on the bottom of the titration vessel; the connection was made with a Pt needle. Air was expelled from all cells by *nitrogen* gas, purified according to Meyer and Ronge [9].

The cells were kept in a paraffin oil thermostat at $25.0 \pm 0.1^\circ \text{C}$. E was measured with a Vernier compensator and a Multiflex galvanometer type MG 2. A Leeds & Northrup amplifier was also used for cells with a high resistance.

Procedure

Parallel experiments were made with perchlorate and nitrate media. In some series, x'' was varied by titration, and in others "fixed cells" were used.

In the *titrations*, the buret solution had the same c_a , or c_1 , or c_1 and c_2 , and moreover $[\text{H}^+] = 0.010 \text{ M}$, as the original solution in the titration vessel (right-hand half-cell), but a higher or lower value of x . The closed part of the cell contained a silver electrode, always with $c_a = 0.010 \text{ M}$ and $x' = 1 \text{ M}$. In titrations with B or C cells, the emf usually attained a constant value within a few minutes after each addition of solution; with cells of type A, 10–20 minutes were sometimes required.

With *fixed cells*, E became constant after about 30 minutes; this is probably the time needed for temperature adjustment after making up the cell.

Variation of liquid-junction potentials

In most of our experiments, both in the titrations and the fixed cells, the liquid junction was as the tip of the J-shaped end of a salt bridge inserted into the open (titration) vessel (see e.g. Fig. 1 a in Biedermann and Sillén [8]). Our assumption (7) was supported by the fact that we obtained concordant results with fixed cells, and with titrations, either increasing or decreasing x'' . How-

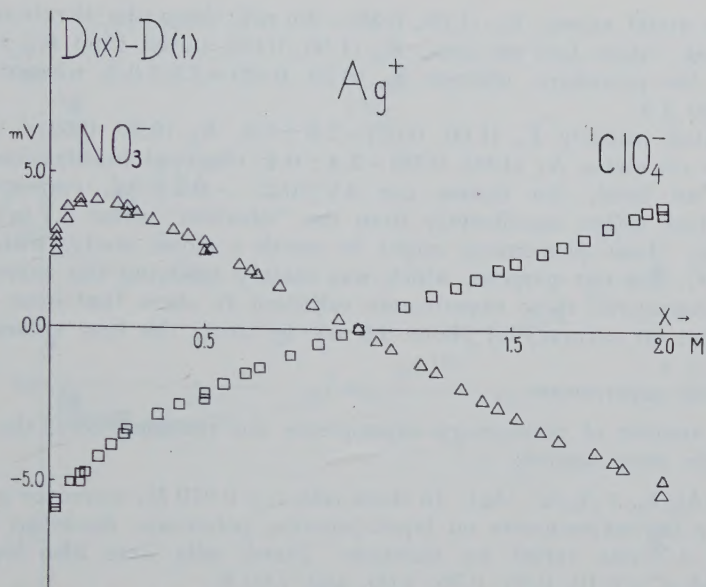


Fig. 1. Deviation function $D_a(x) - D_a(1)$, eq. (16 a), for Ag^+ in nitrate (Δ) and perchlorate ($\square$) media, calculated using (20 a).

ever, for cells with values of x less than 0.1 M, deviations of up to 1 mV were observed. In this region, E also varied slightly with time.

Since the diffusion layer between solutions x'/x'' as different as 1.00/0.02 seemed to be somewhat unstable, we made a special study of cells where the diffusion layer could be renewed at will. We made a special "Wilhelm" apparatus, where the T-shaped three-way stop-cock was so turned that, when the connection was closed, the straight connecting tube was vertical, and the unused branching tube horizontal. Now, the diffusion layer was placed in this three-way stop-cock, with the heavier solution below, and was renewed at will by flushing with both solutions according to various procedures.

Values obtained from B and C cells with this type of connection are marked with circles in the figures (half-full $\circ$ for NO_3^- , full $\bullet$ for ClO_4^-).

We studied especially cells of type A, with $x'/x'' = 1.00/0.02$ or $0.30/0.02$ in the junction. If (7) were correct, the difference between the E measured for two such cells would be equal to E_A for a cell with 1.00/0.30, which was well-known from previous titration experiments.

Cells with 0.30/0.02 were found to give a rather stable emf, which changed only by a few 0.1 mV in half an hour, and did not seem to depend on how the junction was prepared. With 1.00/0.02, the emf measured immediately after flushing with both solutions was rather independent of the flushing scheme used. It changed with time, however, and the values obtained could differ by 1 mV, depending on e.g. how narrow a slit was kept open in the stop-cock.

The values found with a fresh junction were found to agree well with each other and with E_A (1.00, 0.30), and in the following the initial values were used. For perchlorates, the initial values were E_A (1.00, 0.02) = 5.8, E_A (0.30, 0.02) = 2.8 mV,

whence one would expect $E_A(1.00, 0.30) = 3.0$ mV; from the titrations, 3.1 mV was obtained. After half an hour, $E_A(1.00, 0.02)$ varied from 5.2 to 6.1, depending on the procedure, whereas $E_A(0.30, 0.02) = 2.6 \pm 0.2$, whence $E_A(1.00, 0.30) = 2.6$ to 3.5.

For nitrates: initially $E_A(1.00, 0.02) = 2.9 \pm 0.3$, $E_A(0.30, 0.02) = -0.5 \pm 0.2$, whence one calculates $E_A(1.00, 0.30) = 3.4 \pm 0.4$; observed in titrations 3.7 mV. After half an hour, the figures are 3.9 ± 0.2 , -0.7 ± 0.2 , corresponding to 4.6 ± 0.3 , which differs significantly from the "titration" value 3.7 mV.

Of course, these phenomena might be worth a closer study, with variation of c_a and h . For our purpose, which was mainly studying the variation of K in (1), we considered these experiments sufficient to show that even for low x'' one could get an accuracy of about 0.5 mV by using the first values.

Survey of the experiments

After a number of preliminary experiments not recorded here, the following series of cells were studied:

Cells A ($\text{Ag}/c_a, x'/c_a, x''/\text{Ag}$). In these cells $c_a = 0.010$ M; moreover $x' = 1.00$ M, except for a few experiments on liquid-junction potentials, described above. In some cells, x'' was varied by titration. Fixed cells were also studied with $x' = 1.00$ and $x'' = 0.10, 0.25, 0.50, 1.00$, and 2.00 M.

Cells B ($\text{Ag}/c_a, x'/c_1, x''/\text{Hg}$) with $c_a = 0.010$ and $c_1 = 0.010, 0.002$, or 0.001 M. In one series of data (open symbols), x' was kept constant = 1 M, whereas x'' was varied by titration. In another series (full symbols), we had $x' = x'' = x$, with $x = 0.02, 0.10, 0.25, 0.50, 1.00$, or 2.00 M.

Cells C ($\text{Ag}/c_a, x'/c_1, c_2, x''/\text{Pt}$) with $c_a = 0.010$ and $c_1 = c_2 = 0.005, 0.002$, or 0.001 M. In the titrations, x' was always = 1 M; in another set of experiments, with $x' = x'' = x$, x was chosen as 0.02, 0.10, 0.25, 0.50, 1.00, or 2.00 M.

Figures 1-10 give the experimental data, treated in various ways. Sometimes a point is an average of two determinations; in general, however, parallel experiments were carried out at two different sets of values for $c_1(c_2)$. In the figures, black symbols stand for fixed cells with $x' = x''$, and open symbols for other cells (usually titration data). Triangles are for nitrate data (Δ at higher, ∇ at lower $c_1(c_2)$), and squares for perchlorate experiments ($\square$ for higher, $\diamond$ for lower values of $c_1(c_2)$).

Tables 1 and 2 give the values of E and E^* for fixed cells, at the six x values used, compared with the corresponding values found with titration. The values are seen to differ but little, except at the very low values of x .

The deviation functions $D(x)$

The deviation functions $D(x)$ have been so defined as to be zero at $x = 0$. Since the extrapolation to $x = 0$ is somewhat uncertain, whereas the cells with $x'' = 1$ are very stable, the function $D(x) - D(1)$ was first calculated, using equations (20-22).

The function $D(x) - D(1)$ is given for Ag^+ in Fig. 1, for Hg_2^{2+} in Fig. 2, and for Hg^{2+} in Fig. 3. By extrapolation of $D(x) - D(1)$ to $x = 0$, one gets approximate values for $D(1)$ (since $D(0) = 0$, eq. 16 e). These values have been used for drawing the curves $D(x)$ in Fig. 4 and Fig. 5.

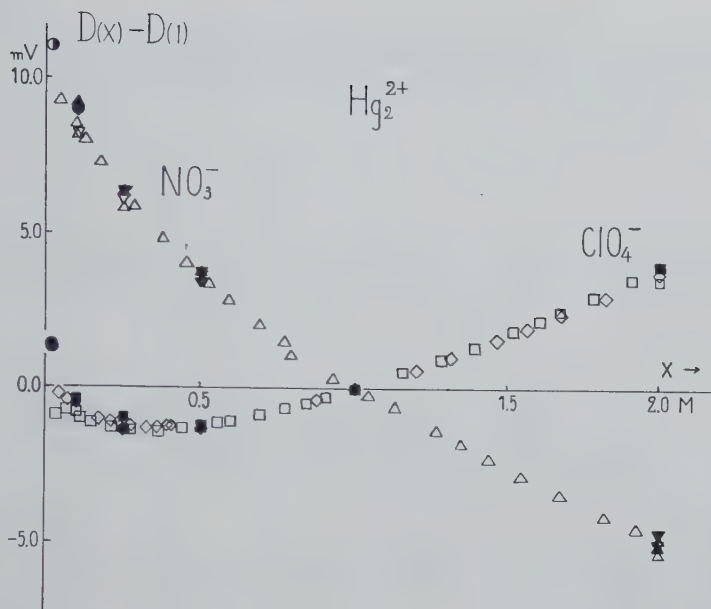


Fig. 2. Deviation function $D_1(x) - D_1(1)$, eq. (16 b), for Hg_2^{2+} in nitrate (triangles) and perchlorate (squares) media, calculated using 21 a (fixed cells, black symbols) or 21 b (titration, open symbols). $c_1 = 0.010$: $\square$, $\triangle$; $c_2 = 0.001$: $\diamond$, ∇ . Circles: special cells, see p. 111.

As seen from (16), one may imagine $D(x)$ as made up of three terms: one for the Coulomb-force activity factor f , one for the complex formation, and one for the liquid junction.

The *liquid-junction* term $e_j(x)$ should always be positive, since both ClO_4 and NO_3 have a higher ionic conductance than Na^+ . The dotted curve in Fig. 4 gives the $e_j(x)$ calculated using the Henderson equations, (7), and (7 a)

$$e_j(x) = 59.16 \left(\frac{l_x - l_{\text{Na}}}{l_x + l_{\text{Na}}} \right) \log \left[1 + x \left(\frac{l_{\text{Na}} + l_x}{h(l_{\text{H}} - l_{\text{Na}})} \right) \right] \approx 8.96 \log (1 + 51.4 x) \quad (27)$$

The numerical values are calculated from the ionic conductance at infinite dilution [10] for Na^+ (50.1), H^+ (349.7), and ClO_4 (68.0) at 25°C . The curve for NO_3 ($l = 71.4$) [10], calculated in the same way, differs only by 1–2 mV. The transference numbers in NaX may not be expected to vary very much with the concentration, so this curve may indicate the order of magnitude.

The *activity factor* term in (16) can be expected first to be negative, to pass through a minimum, and finally to change sign and become positive. The *complexity* term should always give a negative contribution.

In Fig. 4, the curves for Hg_2^{2+} and Ag^+ in ClO_4 solutions are roughly what one might expect, if there were no complex formation but only liquid-junction potential and activity factors to consider. The difference between the two curves

Table 1. Extract of emf data for cells with perchlorate ions. In all solutions, $h = [\text{H}^+] = 0.010 \text{ M}$. In all silver half-cells (both sides in cells A, left hand in cells B and C), $c_a = 0.010$ if not otherwise stated.

	$x = 2.00$	1.00	0.50	0.25	0.10	0.02
Cells A (1, x)						
$c_a = 0.010$; fixed, $E = E^* =$	3.78	0.00	$\begin{cases} -2.34 \\ -2.14 \end{cases}$	$\begin{cases} -3.31 \\ -3.35 \end{cases}$	$\begin{cases} -4.82 \\ -4.73 \end{cases}$	$\begin{cases} -5.70 \\ -5.77 \end{cases}$
Same, titr.	4.09	0.00	-2.15	-3.40	-4.82	
Cells B (1, x), titr.						
$c_1 = 0.001$ $E =$	19.60	15.78		14.60	15.25	
$E^* =$	-9.98	-13.80		-14.98	-14.33	
$c_1 = 0.010$ $E =$	49.48	45.40	44.20	44.06	44.45	
$E^* =$	-9.68	-13.76	-14.96	-15.10	-14.71	
Cells B (x , x), fixed						
$c_1 = 0.00094$ $E =$		15.45	16.19	17.40	19.72	
$c_a = 0.0099$ $E^* =$		-13.60	-12.86	-11.65	-9.33	
$c_1 = 0.001$ $E =$						22.7, 22.8
$c_a = 0.01003$ $E^* =$						-6.79, -6.69
$c_1 = 0.002$ $E =$						31.7, 31.8
$c_a = 0.01003$ $E^* =$						-6.70, -6.60
Cells C (1, x), titr.						
$c_1 = 0.001$ $E =$	163.47	147.22		135.10	132.85	
$c_2 = 0.001$ $E^* =$	133.89	117.64		105.52	103.27	
$c_1 = 0.005$ $E =$	184.53	168.05	160.14	155.70	153.20	
$c_2 = 0.005$ $E^* =$	134.28	117.79	109.88	105.44	102.94	
Cells C (x , x), fixed						
$c_1 = 0.00094$ $E =$		148.91	142.69	140.44	139.01	
$c_2 = 0.001$ $E^* =$		118.28	112.06	109.81	108.38	
$c_1 = c_2 = 0.001$ $E =$						137.2, 137.3
$c_a = 0.01003$ $E^* =$						107.71, 107.81
$c_1 = c_2 = 0.002$ $E =$						146.3, 146.7
$c_a = 0.01003$ $E^* =$						107.90, 108.30

is in the right direction, although its exact amount at the lowest x is not too certain.

However, the difference between the Hg_2^{2+} curve and the two others in Fig. 4 seems greater than one would expect with only Coulomb-force activity factors. One is led to suspect that there may be some specific interaction, which one might describe as a complex formation between Hg_2^{2+} and ClO_4^- .

Fig. 5, for the nitrate solutions, indicates complex formation in all cases; one would expect both the Coulomb-force activity factor and the e_j to be roughly the same in NO_3^- and ClO_4^- solutions.

Table 2. Extract of data for cells with nitrate ions. In all solutions, $h = 0.010$ M. At all silver electrodes (both sides in cells A, left-hand in cells B and C), $c_a = 0.010$ M if not otherwise is stated.

	$x = 2.00$	1.00	0.50	0.25	0.10	0.02
Cells A (1, x)						
$c_a = 0.010$, fixed, $E = E^* =$	— 4.89	0.00	$\begin{Bmatrix} 2.40 \\ 2.77 \end{Bmatrix}$	$\begin{Bmatrix} 3.96 \\ 3.86 \end{Bmatrix}$	$\begin{Bmatrix} 4.16 \\ 4.11 \end{Bmatrix}$	2.88, 3.06, 3.13
Same, titr.	— 5.38	0.01	2.75	3.90	4.00	
Cells B (1, x), titr.						
$c_1 = 0.001$ $E =$	8.87	13.96	17.64	20.07	22.20	
$E^* =$	— 20.71	— 15.62	— 11.94	— 9.51	— 7.38	
$c_1 = 0.010$ $E =$	38.15	43.59	41.87	48.02	50.40	
$E^* =$	— 21.01	— 15.57	— 17.29	— 11.14	— 8.76	
Cells B (x , x), fixed						
$c_1 = 0.001$ $E =$	14.21	14.01	15.01	16.45	18.78	22.1, 22.2 ¹
$E^* =$	— 15.37	— 15.57	— 14.57	— 13.13	— 10.80	— 7.48, — 7.38
$c_1 = 0.002$ } $E =$					27.7	
$c_a = 0.01003$ } $E^* =$					— 10.70	
$c_1 = 0.010$ $E =$	43.40	43.64	44.71	46.03	48.74	
$E^* =$	— 15.76	— 15.52	— 14.45	— 13.13	— 10.42	
Cells C (1, x) titr.						
$c_1 = c_2 = 0.001$ $E =$	132.76	133.48	134.90	136.28	137.72	
$E^* =$	103.18	103.90	105.32	106.70	108.14	
$c_1 = c_2 = 0.005$ $E =$	153.72	154.03	155.32	156.70	158.05	
$E^* =$	103.46	103.77	105.06	104.44	107.79	
Cells C (x , x), fixed						
$c_1 = c_2 = 0.001$ $E =$	138.01	133.53	132.35	132.16	133.55	136.3, 136.4
$E^* =$	108.43	103.95	102.77	102.58	103.97	106.72, 106.82
$c_1 = c_2 = 0.002$ } $E =$						142.4, 142.5
$c_a = 0.01003$ } $E^* =$						104.0, 104.1
$c_1 = c_2 = 0.005$ $E =$	159.00	154.08	152.62	153.04	154.60	
$E^* =$	108.74	103.82	102.36	102.78	104.34	
						¹ $c_a = 0.01003$

Estimates of complexity products

We shall now estimate the complexity products on the tentative assumption that there is no complex formation between Hg^{2+} and ClO_4^- , and that $D_{2h}(x)$ is negligible, so that, from (16 c)

$$D_2(x, \text{ClO}_4^-) = 29.58 \log f_2(x) + e_j(x) \quad (28)$$

We shall moreover assume that this function $D_2(x, \text{ClO}_4^-)$ gives approximately the activity + liquid-junction terms also for Hg_2^{2+} in NO_3^- medium, and like-

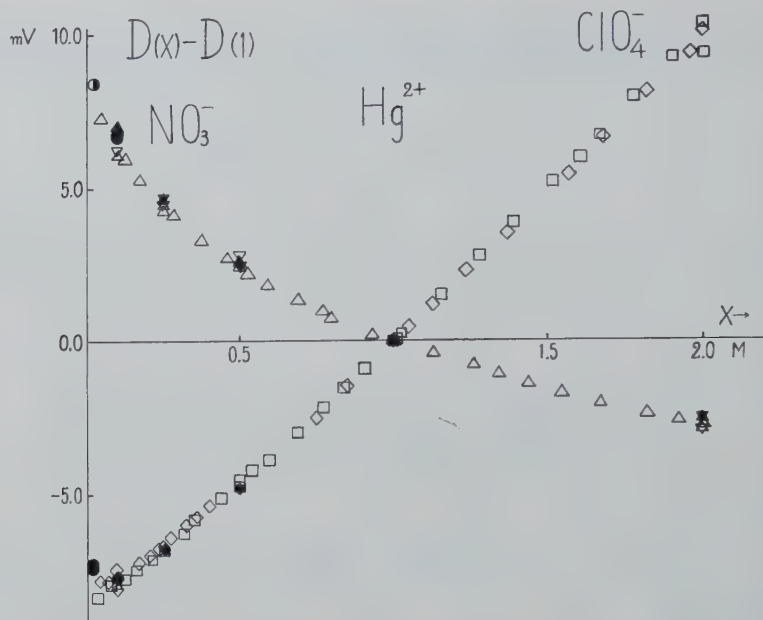


Fig. 3. Deviation function $D_2(x) - D_2(1)$ for Hg^{2+} in nitrate (triangles) and perchlorate (squares) media, calculated using 22 a (fixed cells, black symbols) or 22 b (titration, open symbols). $c_1 = 0.010$ in B, $c_1 = c_2 = 0.005$ in C: $\square, \triangle$; $c_1 = c_2 = 0.001$: $\diamond, \nabla$. Circles: other cells, see p. 111.

wise for the bipoisitive Hg_2^{2+} in ClO_4^- or NO_3^- medium. Then, we may estimate the complexity products β_n by calculating:

$$\text{antilog} \left[\frac{D_2(x, \text{ClO}_4^-) - D_2(x, \text{NO}_3^-)}{29.58} \right] = 1 + \beta_1 x + \dots \text{ for } \text{Hg}^{2+} - \text{NO}_3^- \quad (29 \text{ a})$$

$$\text{antilog} \left[\frac{D_2(x, \text{ClO}_4^-) - D_1(x, \text{NO}_3^-)}{29.58} \right] = 1 + \beta_1 x + \dots \text{ for } \text{Hg}_2^{2+} - \text{NO}_3^- \quad (29 \text{ b})$$

$$\text{antilog} \left[\frac{D_2(x, \text{ClO}_4^-) - D_1(x, \text{ClO}_4^-)}{29.58} \right] = 1 + \beta_1 x + \dots \text{ for } \text{Hg}_2^{2+} - \text{ClO}_4^- \quad (29 \text{ c})$$

These expressions were calculated, using the $D(x)$ curves in Figs 4 and 5, and plotted as functions of x (Fig. 6 a and 6 b). The curves are seen to approach 1.0 with decreasing x , which gives some confidence in the extrapolation of D_1 and D_2 in Figs. 1-3. The upward trend in the curves may be attributed to the formation of a second complex, HgX_2 , which would give a second-degree term $\beta_2 x^2$. However, β_1 and the other complexity products are functions of x , since they contain a number of activity factors. Since no accurate way of differentiating between the variation of β_1 and the effect of a second complex is apparent, we have restricted ourselves to calculating, as a rough estimate, an average first complexity product $\beta_1 = [\text{HgX}^+]/[\text{Hg}^{2+}][\text{X}^-]$ or correspondingly for Hg_2^{2+} , neglecting all higher complexes. The results are:

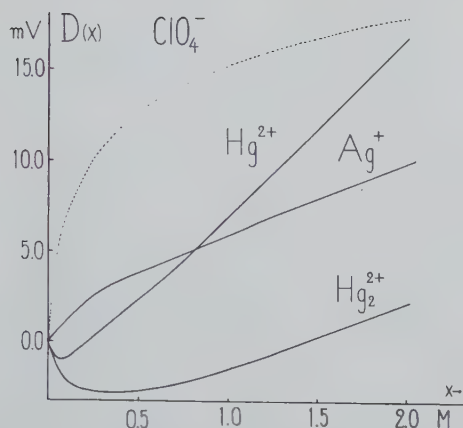


Fig. 4. Deviation functions $D(x)$ for Ag^+ , Hg_2^{2+} , and Hg^{2+} in perchlorate medium. Smoothed curves from Figs. 1-3, displaced parallel after extrapolation to $x=0$. Dotted curve: roughly estimated e_j from (27).

$$\text{Hg}^{2+}\text{-NO}_3^- \quad \beta_1 \approx 2.25 \text{ M}^{-1} \quad (30 \text{ a})$$

$$\text{Hg}_2^{2+}\text{-NO}_3^- \quad \beta_1 \approx 2.5 \text{ M}^{-1} \quad (30 \text{ b})$$

$$\text{Hg}_2^{2+}\text{-ClO}_4^- \quad \beta_1 \approx 0.9 \text{ M}^{-1} \quad (30 \text{ c})$$

For $\text{Hg}_2^{2+}\text{-NO}_3^-$ in 3 M NaClO_4 medium at 25°C , Infeldt and Sillén [2] found $\beta_1 \approx 1.28 \text{ M}^{-1}$ and $\beta_2 \approx 1.0 \text{ M}^{-2}$, which would give a curve not so far from our rough estimate above. For $\text{Hg}_2^{2+}\text{-NO}_3^-$, they gave, neglecting the complex formation with ClO_4^- , $\beta'_1 = 1.2 \text{ M}^{-1}$ in 0.5 M NaClO_4 , and $\beta'_1 = 1.05 \text{ M}^{-1}$, $\beta'_2 = 0.5 \text{ M}^{-2}$ in 3.0 M NaClO_4 . Correspondingly we may calculate

$$\text{antilog} \left[\frac{D_1(x, \text{ClO}_4^-) - D_1(x, \text{NO}_3^-)}{29.58} \right] = 1 + \beta'_1 x + \dots \text{ for } \text{Hg}_2^{2+}\text{-NO}_3^-(\text{ClO}_4^-) \quad (29 \text{ d})$$

This curve is also given in Fig. 6 b; neglecting β'_2 we find an average $\beta'_1 \approx 1.2 \text{ M}^{-1}$, which agrees fairly well with the values of Infeldt and Sillén.

We should like to point out here that in the discussion of the sulfate complexes, Infeldt and Sillén have introduced an error by neglecting the formation of HSO_4^- .

We may also try to calculate the complex formation $\text{Ag}^+\text{-NO}_3^-$, assuming that Ag^+ and ClO_4^- form no complexes, and that $D_a(x, \text{ClO}_4^-) = e_j(x) + 59.16 \log f_a(x)$ is applicable also in NO_3^- medium. Then

$$\text{antilog} \left[\frac{D_a(x, \text{ClO}_4^-) - D_a(x, \text{NO}_3^-)}{59.16} \right] = 1 + \beta_1 x + \dots \text{ for } \text{Ag}^+\text{-NO}_3^- \quad (29 \text{ e})$$

From the $D_a(x)$ in Figs. 4 and 5 we have calculated the expression (29 e); this is the lower curve in Fig. 6 c, which, however, tends towards a value

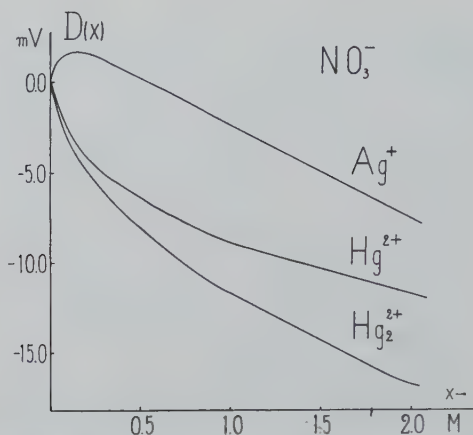


Fig. 5. Deviation functions $D(x)$ for Ag^+ , Hg_2^{2+} , and Hg^{2+} in nitrate medium. Smoothed curves from Figs. 1–3, displaced parallel after extrapolation to $x=0$.

around 0.90 rather than 1.00 as $x \rightarrow 0$. Correspondingly, $D_a(x, \text{ClO}_4) - D_a(x, \text{NO}_3)$ does not tend to 0 but to about -2.2 mV. Assuming that this is an error arising from the extrapolation of the $D_a(x) - D_a(1)$ data in Fig. 4 or 5, we have multiplied the original values in the function (29 e) by $\text{antilog}(2.2/59.16) = 1.09$, which gives the upper curve in Fig. 6 c. From the points for $x=0$ to 1 M we find an average β_1 of 1.0 M^{-1} for $\text{Ag}^+ - \text{NO}_3^-$.

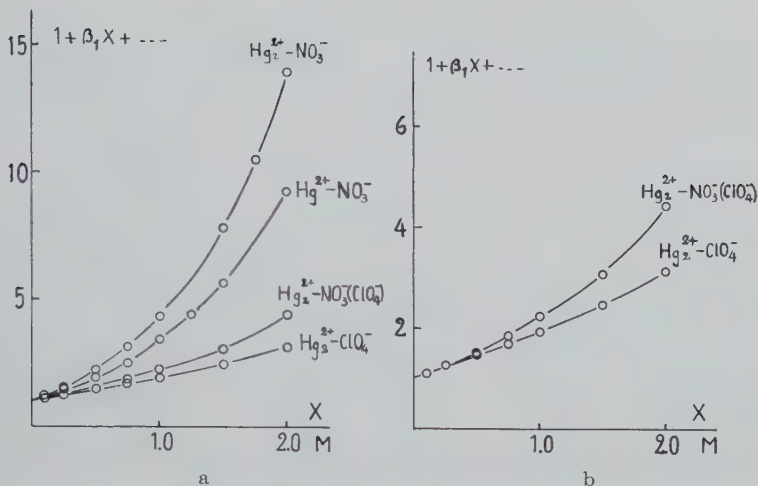
Earlier estimates are 0.46 M^{-1} (Ölander and Adelson [11]) and about 2 M^{-1} (Robinson and Stokes [12]).

Whatever be the cause of the deviations in the D_a functions, in the following calculations of K and e^0 , we have only used the more accurate $D_a(x) - D_a(1)$ from Fig. 1, and not the $D_a(x)$ values from Figs. 4 and 5. The extrapolations in Figs. 7–10 are consequently independent of any error arising from the extrapolations in Figs. 1–3.

The equilibrium constant K

Fig. 7 a gives $59.16 \log K(x)$, calculated according to (26); in Fig. 7 b the data for the lowest concentrations are shown on an enlarged scale. As before, the black symbols represent fixed cells with $x' = x'' = x$ (26 b), and the open symbols the titration cells with $x' = 1$ (26 a); triangles represent nitrate data, and squares perchlorate experiments. For each of the anions, concordant values were obtained (as with our other data) with "fixed" and with titration cells, both increasing and decreasing x , and also with different sets of values for c_1 and c_2 . This seems to indicate that the liquid-junction potentials are really eliminated in our calculations.

On first sight it is remarkable that K varies much more with x for ClO_4^- than for NO_3^- . However, it is readily understood in view of the previous data, if it is assumed that the activity factors of the two bipovalent ions Hg_2^{2+} and



Figs. 6 a and b. Approximate complexity functions for $\text{Hg}_2^{2+}-\text{NO}_3^-$ (29 a), $\text{Hg}_2^{2+}-\text{NO}_3^-$ (29 b), $\text{Hg}_2^{2+}-\text{ClO}_4^-$ (29 c), and $\text{Hg}_2^{2+}-\text{NO}_3^-(\text{ClO}_4^-)$ (29 d).

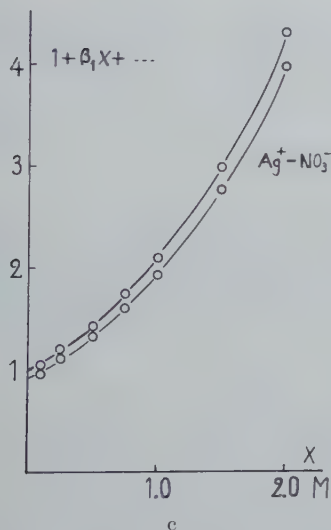


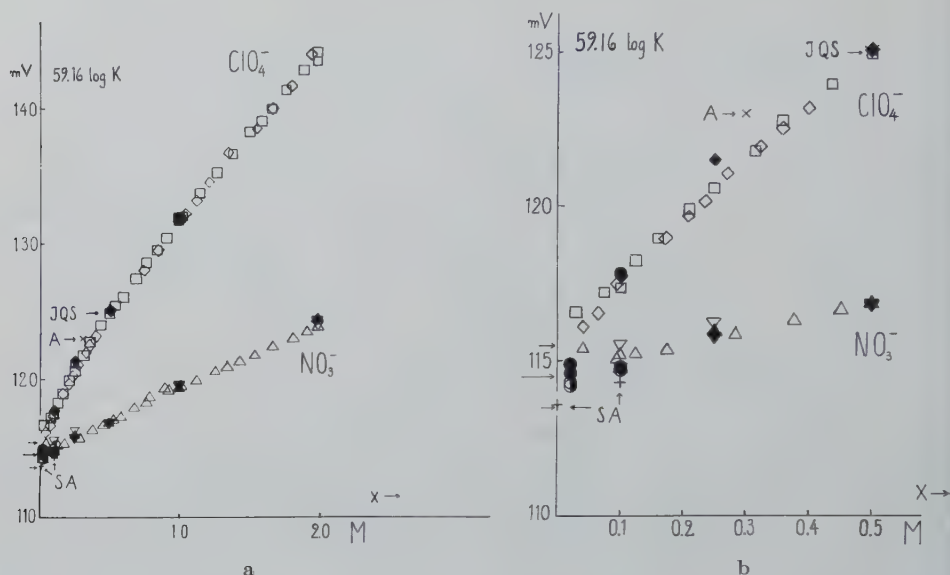
Fig. 6 c. Approximate complexity functions for $\text{Ag}^+-\text{NO}_3^-$, calculated by means of (29 e). Lower curve: using curve in Fig. 5. Upper curve: corrected by multiplication with 1.09.

Hg_2^{2+} are roughly equal, and that they form nitrate complexes of approximately the same strength, whereas Hg_2^{2+} forms stronger ClO_4^- complexes than does Hg^{2+} .

As expected, the measurements for both media give the same value on extrapolation

$$59.16 \log K(x=0) = 114.5 \pm 1.0 \text{ mV} = e_{21}^{0'} - e_{10}^0 \quad (31)$$

In the extrapolation, somewhat higher weight has been given to the two points corresponding to fixed cells with $x' = x'' = 0.02$ than to some neighboring points.



Figs. 7 a and b. $59.16 \log K$, calculated with (26 a) or (26 b) as a function of anion concentration x in perchlorate and nitrate media, with $h = [\text{H}^+] = 0.010$ M. K = apparent equilibrium constant for $\text{Hg}^{2+} + \text{Hg}(\text{l}) \rightleftharpoons \text{Hg}_2^{2+}$. Previous data: SA [6], JQS [4], A [3]. Black symbols: "fixed cells" with $x' = x'' = x$. Open symbols: titration cells with $x' = 1$. Nitrate data: Δ for $c_1 = 0.010$ M in B cells, $c_1 = c_2 = 0.005$ M in C cells, ∇ for $(c_1)_B = (c_1)_C = 0.001$ M. Perchlorate data: $\square$ for the higher, $\diamond$ for the lower values of c_1 and c_2 . The arrows to the left give the extrapolated value $59.16 \log K (x=0) = 114.5 \pm 1.0$ mV (31).

However, (31) is valid for a hydrogen ion concentration of 0.010 M, at which acidity the formation of HgOH^+ and $\text{Hg}(\text{OH})_2$ is not quite negligible. To make this small hydrolysis correction, we shall use (17), and assume that the values [1] for 0.5 M NaClO_4 ($pK_{a1}^0 = 3.7$, $pK_{a2}^0 = 2.6$) are also valid at infinite dilution

$$\begin{aligned} e_{21}^0 &= e_{21}^{0'} + 59.16 \log (1 + 0.01^{-1} \cdot 10^{-3.7} + 0.01^{-2} \cdot 10^{-6.3}) \\ &= e_{21}^{0'} + 59.16 \log 1.025 = e_{21}^{0'} + 0.6 \text{ mV} \end{aligned} \quad (17 \text{ a})$$

Hence

$$59.16 \log K^0 = 115.0 \pm 1.0 \text{ mV} = e_{21}^0 - e_{10}^0 \quad (32)$$

$$K^0 = 88 \pm 4 \quad (32 \text{ a})$$

Previous measurements are also shown in Fig. 7: JQS is the value given by Jonsson, Qvarfort, and Sillén [4] for the 0.5 M perchlorate medium, SA are two crosses corresponding to Schwarzenbach's and Anderegg's values [6] for nitrate media. The JQS point coincides exactly with our present data, the SA points are slightly lower. Fig. 7 illustrates very clearly the reasons for the previous apparent discrepancy.

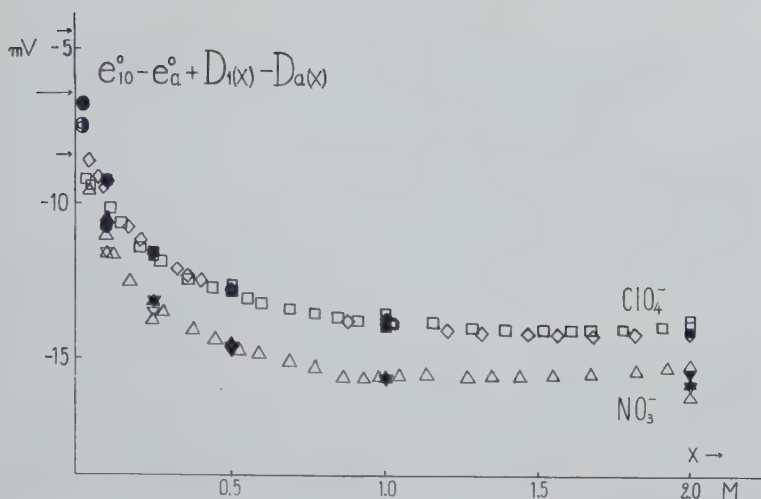


Fig. 8. Plot according to eq. (23). Same symbols as in figs. 2-3 and 6-7. Arrows to the left give extrapolated value $e_{10}^0 - e_a^0 = -6.4 \pm 2.0$ mV (34 a).

Finally, the point A corresponds to the (analytical) equilibrium constant of Abel [3], which should be valid in 0.3 M HNO_3 . It falls very far off the nitrate curve, but this is not surprising considering the analytical difficulties.

The standard potentials e^0 .

Figs. 8, 9, and 10 give plots according to equations (23), (24), and (25), which should give, by extrapolation to $x=0$, the differences between e_{10}^0 , $e_{21}^{0'}$, and $\frac{1}{2}(e_{10}^0 + e_{21}^{0'})$ and the standard potential e_a^0 of Ag^-/Ag . The value of the latter may be taken from Owen and Brinkley [13], recalculated [14] to absolute mV:

$$e_a^0 = 799.4 \pm 0.2 \text{ mV} \quad (33)$$

The extrapolations are somewhat uncertain; at the lowest concentrations, one should probably give more weight to the fixed cells, i.e. to the black symbols. If a very accurate extrapolation were desired, one might use cells of the same types as here, but also vary h and c_a . Even from the present data, which were primarily designed to give the values for K , one may estimate the following extrapolated values:

$$e_{10}^0 - e_a^0 = -6.4 \pm 2.0; \quad e_{10}^0 = 793.0 \pm 2.0 \text{ mV} \quad (34 \text{ a})$$

$$e_{21}^{0'} - e_a^0 = 107.6 \pm 1.0 \text{ mV}; \quad e_{21}^{0'} = 907.0 \pm 1.0 \text{ mV} \quad (34 \text{ b})$$

$$\frac{1}{2}(e_{21}^{0'} + e_{10}^0) - e_a^0 = 50.6 \pm 1.5 \text{ mV}; \quad \frac{1}{2}(e_{21}^{0'} + e_{10}^0) = 850.0 \pm 1.5 \text{ mV} \quad (34 \text{ c})$$

These values agree well with (31), $e_{21}^{0'} - e_{10}^0 = 114.5 \pm 1.0$ mV.

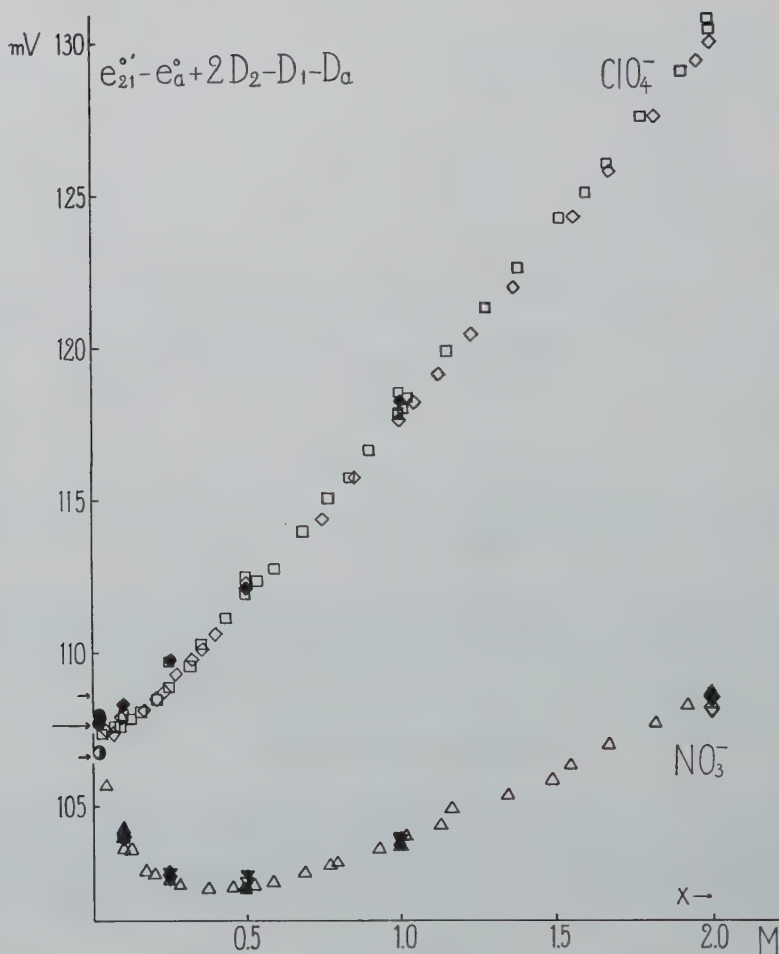


Fig. 9. Plot according to eq. (24). Same symbols as in previous Figs. Arrows to the left give extrapolated $e_{21}^{\circ'} - e_a^{\circ} = 107.6 \pm 1.0$ mV (34 b).

We would propose as best values for 25°C ;

$$e_{10}^0 = e^0(\text{Hg}_2^{2+}/\text{Hg}) = 792.5 \pm 1.0 \text{ mV} \quad (35 \text{ a})$$

$$e_{21}^{\circ'} = 907 \pm 1 \text{ mV}; \quad e_{21}^0 = e^0(\text{Hg}_2^{2+}, \text{Hg}_2^{2+}/\text{Pt}) = 907.5 \pm 1.0 \text{ mV} \quad (35 \text{ b})$$

In previous measurements of e_{21}^0 and e_{10}^0 there have been difficulties with the extrapolation, which have been discussed in some detail by Berecki, Biedermann, and Sillén [15].

The data of Linhart 1916 have been extrapolated to $e_{10} = 792.6$ mV by Linhart himself [16], to 798.6 mV by Lewis and Randall 1923, to 797.5 mV by

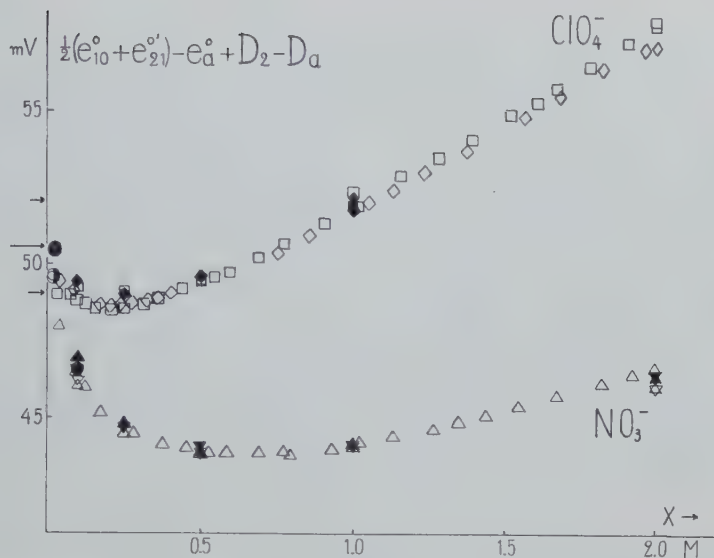


Fig. 10. Plot according to eq. (25). Same symbols as in previous Figs. Arrows to the left give extrapolated value $\frac{1}{2}(e_{21}^{0'} + e_{10}^0) - e_a^0 = 50.6 \pm 1.5$ mV (34 c).

Bray and Hershey 1934, and to 793.0 mV by Law 1946 [15]. Christensen [17] has used cells of the same type as Linhart,



Using only the points for higher concentrations, he found $e_{10}^0 = 792$ mV, whereas extrapolation from the two lowest concentrations used gave 778.3 mV.

Recently, Bonner and Unietis [18] have extrapolated the value 796.1 mV from cells with mercury and glass electrodes.

For e_{21}^0 , Carter and Robinson [19] have given 913 mV, and Popoff and co-workers obtained 905 mV [20]; Latimer [21], by another extrapolation of Popoff's data, found values around 915 mV.

On the ionic medium principle

The assumption that Hg_2^{2+} forms much stronger complexes with ClO_4^- than does Hg^{2+} seems to give the simplest explanation of the present experimental material.

If this is so, it might at first sight arouse some doubt about the ionic medium principle. In the work on equilibria in NaClO_4 medium that has been carried out in this laboratory and in many others, it has been tacitly assumed that one may neglect the complex formation between ClO_4^- and various cations. One might ask whether the usual way of computing complexity constants is still permissible in cases where perchlorate complexes are formed.

However, one must remember that in studying, say, the equilibria between a metal ion M , a ligand A , and various complexes MA_n , it is not possible to distinguish between species that contain different amounts of the medium molecules. For instance, in NaClO_4 medium the quantity called " $[\text{MA}_2]$ " is really the sum of the concentrations of all complexes $\Sigma [\text{MA}_2(\text{Na})_s(\text{ClO}_4)_t(\text{H}_2\text{O})_u]$. The same applies to any other species. If this is understood, one may still compute and discuss equilibrium constants for reactions between the species " M ", " A ", and " MA_n ". This point has been stressed by Leden [22].

A similar case is the equilibrium $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ in aqueous solution, which cannot easily be measured, so that all the uncharged molecules in aqueous solution are considered as " H_2CO_3 ".

In using an ionic medium, one has the great advantage that the activity factors of various species can be assumed to be constant; this is a necessary condition for evaluating complicated equilibria. The price one has to pay for this advantage is that equilibrium measurements alone will not allow one to draw any conclusion on the equilibria with the solvent or the ions of the medium, as long as the medium is kept constant.

Summary

The equilibrium constant K for the reaction $\text{Hg}_2^{2+} + \text{Hg(l)} \rightleftharpoons \text{Hg}_2^{2+}$ in various nitrate and perchlorate media, with $[\text{H}^+] = 0.010 \text{ M}$, has been measured by emf methods. The results are given in Fig. 7; the apparent K varies little with nitrate ion concentration, but increases strongly with perchlorate ion concentration. From studies of several series of cells [5] it appears that Hg_2^{2+} forms stronger complexes with ClO_4^- than does Hg^{2+} . Assuming that the $\text{Hg}_2^{2+}\text{--ClO}_4^-$ complexes can be neglected, the first complexity product β_1 for $\text{Hg}_2^{2+}\text{--ClO}_4^-$ is estimated to be around 0.9 M^{-1} . On the other hand, nitrate ion appears to form stronger complexes, but of about equal strength, with Hg^{2+} ($\beta_1 \approx 2.25 \text{ M}^{-1}$) and Hg_2^{2+} ($\beta_1 \approx 2.5 \text{ M}^{-1}$). The estimates of β_1 are rough and give at most the order of magnitude.

By extrapolation, the following standard potentials were calculated:

$$e^0(\text{Hg}_2^{2+}/\text{Hg}) = 792.5 \pm 1.0 \text{ mV}, \quad e^0(\text{Hg}_2^{2+}, \text{Hg}_2^{2+}/\text{Pt}) = 907.5 \pm 1.0 \text{ mV},$$

both corrected for hydrolysis. At infinite dilution, the equilibrium constant for $\text{Hg}_2^{2+} + \text{Hg(l)} \rightleftharpoons \text{Hg}_2^{2+}$ was found to be $K^0 = 88 \pm 4$, at 25°C .

The present results explain the previous apparent discrepancy between the values of K obtained in Zürich with nitrate [6] and in Stockholm with perchlorate solutions [4, 1, 5]. Actually both sets of data were correct.

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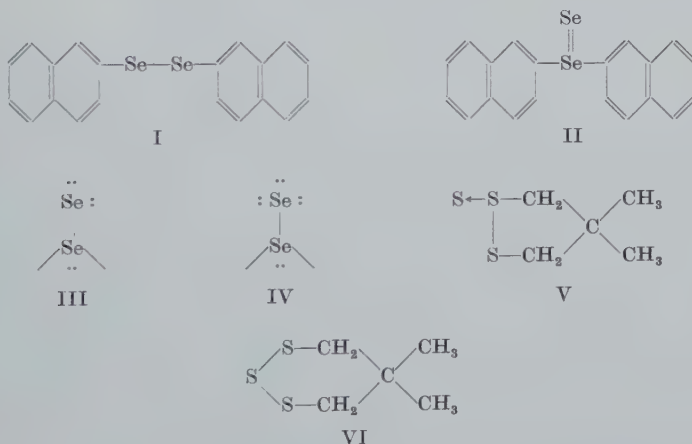


On the hypothetical branched structure of 2,2'-dinaphtyldiselenide

By GÖRAN BERGSON

With 3 figures in the text

As a part of an investigation on diselenides and related compounds, the author has studied some 2-naphtyl derivatives of selenium. Such compounds have a special interest because Loevenich, Fremdling and Föhr (1) describe two substances with a composition corresponding to 2,2'-dinaphtyldiselenide but with different properties. The two substances were assigned the structures I and II. All other diselenides prepared undoubtedly have an unbranched structure like I, and the diselenide with the formula II is, therefore, a very remarkable exception. This was pointed out by Fredga (2) as



early as 1935. At this institute Schotte (3) has recently investigated the structure of some polysulfides, and in this connection it seemed natural to study more closely the selenium compounds mentioned.

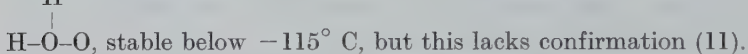
In an unbranched (linear) diselenide each of the two selenium atoms has 8 valence electrons, and the bond between the atoms is typically covalent. For a branched diselenide the two structures III and IV can be postulated. III corresponds to the Loevenich structure II. The most remarkable thing about this structure is that one of the selenium atoms must expand its valence shell to a decet. Spectroscopic investigations by the author (4, 5) have indicated a probable expansion of the selenium

valence shell; however, this refers to electronically excited states of the diselenide molecule. An expansion of the selenium octet in the ground state is, however, very improbable. The sulfur atom only expands its valence shell when bound to strongly electronegative elements, such as oxygen and fluorine, and it is improbable that, in this respect, selenium would differ from sulfur to any great extent. A branched diselenide must therefore possess the structure IV.

Foss (6) has exhaustively discussed the existence and stability of molecules with the branched structure $(R)_x A-B$, where B is a group 6 atom. He shows that molecules of this type are stable only if B is more electronegative than A. Thus, sulfoxides R_2SO , selenoxides R_2SeO , amineoxides R_3NO , phosphineoxides R_3PO , phosphinesulfides R_3PS and phosphineselenides R_3PSe are stable compounds, while molecules of the types R_3NS , R_3NSE , R_2OS , R_2OSE are unknown. (The electronegativities are according to Pauling (7): $O = 3.5$, $N = 3.0$, $S = 2.5$, $Se = 2.4$, $P = 2.1$). Some sulfideselenides R_2S_3Se and selenidesulfides R_2Se_3S are assumed to have a branched structure (8, 9, 10), but the facts on which the structural proof is based, can equally well be explained by a linear structure.

Thus it remains to discuss the stability of molecules where $A = B$ is one of the atoms O, S, Se, Te. Such molecules must also be unstable according to Foss' stability theory, provided the substituents linked to A have not such electronic properties so as to lower the electronegativity of A to a considerable degree.

To begin with oxygen, there has been reported a new form of hydrogen peroxide



Many examples of structural formulae with branched sulfur chains in disulfides, polysulfides and polythionic compounds are to be found in the literature. A very large number of such compounds have been discussed by Foss (6), and have been shown to possess an unbranched structure. The reason for postulating branched structures for those compounds has often been the fact that one or more sulfur atoms can more easily be removed from the molecule than others. Backer and co-workers (12, 13, 14) prepared some cyclic sulfur compounds, to which a branched structure was given. By means of infrared and ultraviolet spectroscopy, and from polarographic studies, Schotte (3) has recently proved that these compounds also contain unbranched sulfur chains. Thus e.g. the compound to which formula V was previously given, has in fact the structure VI. Spectroscopic studies on tetrathiodiglycolic acid also support an unbranched structure (3). X-ray studies on some fluorine substituted di- and polysulfides exclude a branched sulfur chain in these compounds (15). The statement of Baroni (16) that there are two isomeric forms of diethylpentasulfide with branched structure has been proved to be false; the substances prepared are in fact mixtures of linear polysulfides with variable sulfur content (17). Recent experiments with disulfides containing radioactive sulfur also exclude a branched structure for disulfides (18).

Branched selenium chains must, theoretically, be as unstable as the corresponding sulfur structures. No selenium compound hitherto prepared, can with certainty be ascribed such a structure. As has already been mentioned, all diselenides undoubtedly have a linear structure with the exception of one of the forms of 2,2'-dinaphtyldiselenide. It is true that diantipyryldiselenide is also said to possess a branched structure (19, 20), but this assumption is based upon the fact that the compound splits off red selenium when treated with concentrated hydrochloric acid or boiled

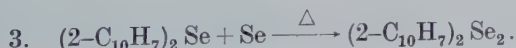
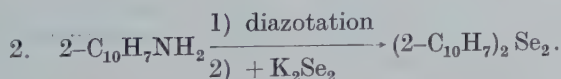
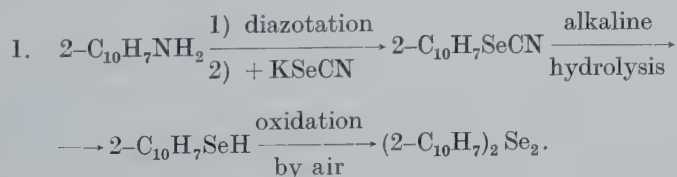
in benzene solution. It is conclusions like this that have caused the erroneous structural formula of many sulfur compounds, and so diantipyryldiselenide is not worth special attention. The same is true of the compounds of the type R_2S_3Se and R_2Se_3S mentioned above.

As to the tellurium compounds prepared, no direct structural proofs are available.

For all sulfur and selenium compounds hitherto studied the question has been to choose between a branched and unbranched structure for one substance. *What gives 2,2'-dinaphtyldiselenide a unique position is the fact that two different substances with the same empirical composition are reported* (1). This justifies a closer study of these compounds.

The substance which, according to Loevenich, has the structure I (hereafter called substance I), consists of yellow crystals melting at $126-127^\circ$, and the substance with structure II (called substance II) is a yellow fine crystalline powder with melting point $112-114^\circ$. These facts can of course be interpreted as polymorphism, but against this stands the fact that the two substances have different properties in solution. Thus, substance I is said to be transformed to 2-naphtylselenol when treated with reducing agents, but is totally indifferent towards oxidation (see also Beilstein Bd. VI. 2. Erg. Bd. p. 614). On the other hand, substance II gives with reducing agents 2,2'-dinaphtylmonoselenide and red selenium. Oxidation of II results in the formation of 2,2'-dinaphtylselenoxide and selenium. On boiling an alcoholic solution of II for a long time, red selenium is deposited in contrast to the behaviour of I. It must, however, be remembered that the chemical properties of II cannot function as definite structural proofs. Diphenyldiselenide, which has a linear structure, also splits off selenium, when its alcoholic solution is kept or evaporated (21).

Substance I has been prepared according to scheme 1. By the oxidation of a selenol, a linear diselenide is undoubtedly formed. The structure of substance I reported in the literature must therefore be true. It should be noted that in this case the method of preparation can function as a structural proof. Rheinboldt and Cecchini (22) have, however, found that this diselenide melts at 139.5° and not at $126-127^\circ$ as Loevenich reports. The author has verified Rheinboldt's and Cecchini's statement, and it is possible that a small amount of selenol has caused the lower m.p. The assertion, mentioned above, that I is stable towards oxidizing agents is very surprising, and the author has found that it is easily affected by e.g. potassium permanganate like all other diselenides. The preparation of substance II follows two methods, which are outlined in reaction formulae 2 and 3.



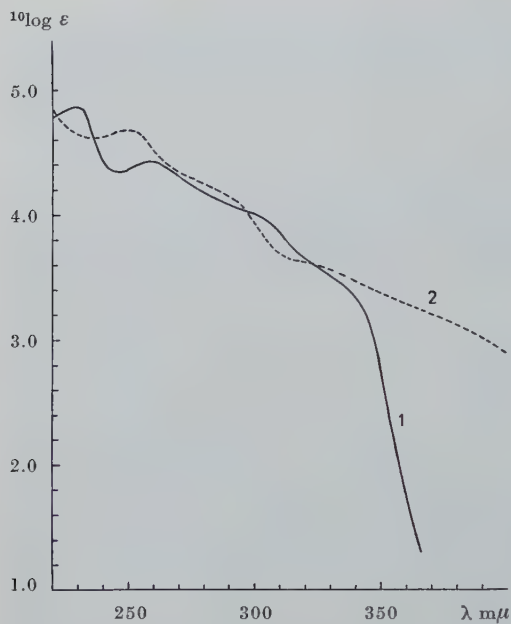


Fig. 1. Ultraviolet absorption of (1) 2,2'-dinaphtylmonoselenide, and (2) 2,2'-dinaphtyldiselenide.

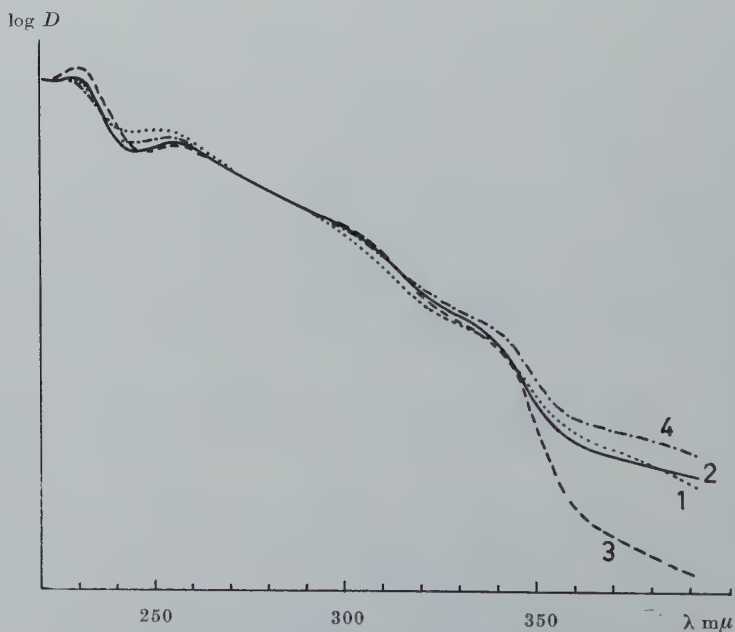


Fig. 2. Ultraviolet absorption of (1) artificial mixture of mono- and diselenide; (2) substance from syntheses *a*; (3) substance from syntheses *b*; (4) substance from syntheses *c*.

The use of alkalidiselenide solutions is one of the standard methods for the preparation of organic diselenides. By this method linear diselenides have always been obtained and therefore it is very surprising that just 2-naphtyldiazoniumchloride should give a branched diselenide. The only complication that arises, and nearly always, in such syntheses, is that monoselenide, too, is formed (23, 24, 25). The synthetic method 3 has been used for the preparation of unbranched diselenides. Thus diphenylmonoselenide and selenium give diphenyldiselenide which has undoubtedly a linear structure (21, 26, 27, 28). The reaction seems to be reversible, for at higher temperatures diselenides decompose into monoselenides and selenium (21, 29). So the synthetic methods used by Loevenich cannot be used as structural proofs for substance II.

In order to get some information about these structural questions the author has repeated Loevenich's experiments and compared the UV-absorption spectra of the substances obtained with the spectra of the linear diselenide and the monoselenide. The absorption spectra of 2,2'-dinaphtyldiselenide (substance I) and 2,2'-dinaphtylmonoselenide in alcoholic solution are shown in Fig. 1. The spectra are very complicated, and a theoretical interpretation would be very difficult. The absorption curve for the diselenide has a maximum at 250 $m\mu$, and inflexions at 285 and 320 $m\mu$. The absorption bands have very high intensity, and the absorption extends to the blue region, which explains the yellow colour of this substance. The monoselenide curve has maxima at 231 and 259 $m\mu$ and inflexions at about 300 and 330 $m\mu$. At 340 $m\mu$ the selective absorption rapidly decreases, and at 370 $m\mu$ the molar extinction coefficient is as low as 10. The monoselenide is colourless.

In three synthetic methods tested by the author, the starting materials have been:

- (a) Diazotized 2-naphtylamine and potassium polyselenide solution.
- (b) Diazotized 2-naphtylamine and potassium diselenide solution.
- (c) 2,2'-dinaphtylmonoselenide and red selenium.

(a) The polyselenide solution was prepared by fusing grey selenium and potassium hydroxide, and then dissolving the product in water (30). The reaction between potassium polyselenide solution and diazotized naphtylamines has been studied by Leicester (31), but he could not isolate any pure substances from the products. Rheinboldt and Giesbrecht (32) have, however, by this method obtained a mixture of di- and monoselenide, from which they prepared pure monoselenide by reducing the diselenide. The present author obtained a fine crystalline yellow substance (m.p. interval 108–115°), which after three recrystallisations from alcohol melted at 119–122° (Liquid drops were, however, observed at somewhat lower temperatures). Fig. 2 curve 2 suggests that this compound is probably a mixture of mono- and diselenide, and this was confirmed by quantitative analysis on selenium. (Curve 1 represents the absorption of an artificial mixture of mono- and diselenide, with about 30 mol % diselenide and m.p. 111–114°.) After treatment with zinc powder in hot glacial acetic acid, addition of water, dissolving the precipitate in chloroform and washing this solution with sodium hydroxide solution, 2,2'-dinaphtylmonoselenide could be isolated in full agreement with Rheinboldt's results. A branched diselenide could therefore not be traced in the reaction products from this experiment.

(b) Potassium diselenide solution was made according to Bird and Challinger (33) by dissolving grey selenium in an aqueous solution of sodium hydroxide and sodium formaldehydesulfoxylate (Rongalit C) in nitrogen atmosphere. This solution was allowed to react with diazotized 2-naphtylamine and the crude product was worked

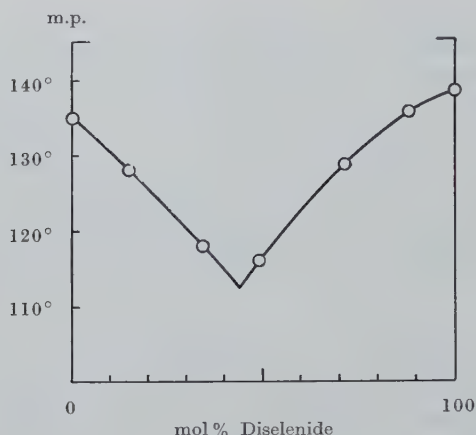


Fig. 3. 2,2'-Dinaphtylmonoselenide and 2,2'-dinaphtyldiselenide.

up according to Loevenich. The substance did not differ considerably from that obtained in a), but after several recrystallisations from alcohol it melted at 129–133°. (Liquid drops were, however, observed at somewhat lower temperatures.) From analysis it was clear that it consisted chiefly of monoselenide, which is also apparent from curve 3, Fig. 2. By reducing the substance according to Rheinboldt, pure monoselenide was isolated. Treatment of the substances from syntheses (a) and (b) with oxidizing agents as well as reducing by Rheinboldt's method did not yield any precipitation of red selenium. Both chemical and spectroscopic observations contradict the statement that a branched diselenide is formed.

(c) On heating 2,2'-dinaphtylmonoselenide (containing a small amount of diselenide as an impurity which, however, cannot influence the results) with red selenium for two days, and after recrystallisation of the product once from alcohol, the author obtained a yellow fine crystalline solid, which melted in the interval 105–115°. During the recrystallisation procedure a very small amount of red selenium separated in accordance with the observation of Loevenich and co-workers. Treatment with potassium permanganate in acetic acid solution gave, however, no selenium. By reducing the yellow acetic acid solution of the substance with zinc dust the solution became colourless (just like the mixtures described above) without any precipitation of selenium. The UV-absorption of the substance is shown in Fig. 2, curve 4. This curve has the same general shape as the curve of the artificial mixture of mono-

Table 1. 2,2'-Dinaphtylmonoselenide; 2,2'-dinaphtyldiselenide (I).

Mol % I	m.p. °C
0.0	135.0
15.0	128.0
34.3	118.0
48.9	116.0
71.6	128.5
88.0	135.5
100.0	138.0

and diselenide, and also closely resembles the curves of the substances from the other experiments. Quantitative analysis on selenium also indicated that this substance is a mixture of mono- and diselenide.

Thus there is nothing in these three experiments that can prove the existence of a branched structure of 2,2'-dinaphtyldiselenide. The low-melting substances described in the literature seem, in view of the above experiments, to consist of mixtures of mono- and diselenide. It should be noted that the mixtures obtained by the author closely resemble the "abnormal" form of the diselenide reported, as regards boiling point, melting point, and general physical properties. The melting point of artificial mixtures of 2,2'-dinaphtyldiselenide and 2,2'-dinaphtylmonoselenide have also been determined by the author. The results are given in Table 1 and Fig. 3.

Experimental

Spectra.—A Beckman model DU photoelectric quartz spectrophotometer equipped with a hydrogen discharge lamp was used for the ultraviolet absorption measurements. All substances were studied in 96 % alcoholic solution at room temperature. The error in wavelength is about $\pm 1 \text{ m}\mu$, and that in the extinction coefficient a few per cent. Beer-Lambert's law is valid for all solutions.

Melting point diagram.—Weighed amounts of the components (total weight 7–10 mg) were dissolved in 1–2 ml of acetone. The solvent was evaporated at room temperature and the residue carefully powdered and dried in vacuum.

2,2'-dinaphtyldiselenide.—This compound was prepared by the oxidation in air of 2-naphtylselenol in ether (1). m.p. 137–138°.

2,2'-dinaphtylmonoselenide.—2-naphtylamine was diazotized in the usual manner with sodium nitrite and excess hydrochloric acid. The solution was buffered with sodium acetate and run into a solution of potassium polyselenide. The solid which precipitated was extracted with ether, the ether removed by distillation, and the resulting product distilled in vacuum (b.p. interval 220–270°). The orange yellow distillate (a solid) was recrystallised three times from alcohol. The resulting substance (m.p. 119–122°) was dissolved in hot glacial acetic acid and treated with zinc dust. The solution was filtered, excess water added, and the white solid which precipitated was taken up in chloroform. This solution was shaken with 10 % sodium hydroxide solution, the chloroform removed by distillation and the resulting product recrystallised from alcohol (32). The monoselenide thus obtained consisted of colourless crystal flakes with m.p. 134–135°.

Summary

Some 2-naphtyl derivatives of selenium have been reinvestigated.

The results indicate that diselenides with branched structure (IV) do not exist. This is in agreement with the general theory of the non-existence of molecules of the type $(R)_x A-B$, when the electronegativity of B is smaller or equal to that of A (6).

The author is indebted to Professor Arne Fredga for suggesting the investigation and for interesting discussions.

Thanks are also due to Dr. Lennart Schotte for his kind interest in this work and for valuable discussions.

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Optically active higher aliphatic hydroxy-compounds

III.¹ Synthesis and configuration of the antipodes of methyl hydrogen β -acetoxyglutarate, key intermediates in the synthesis of optically active β -hydroxy acids²

By KLAUS SERCK-HANSEN

With 1 figure in the text

In continuation of work aiming at the development of general syntheses for optically active long-chain hydroxy-compounds, attention has been turned to methods of making β -hydroxy acids of known configuration.

Optically active normal β -hydroxy acids are of considerable biochemical interest as intermediates in the metabolism of fatty acids (cf. 1, 2.). The C_4 (cf. 3-5), C_6 (6), C_8 (6), C_{10} (7-9), and C_{14} (10) members were isolated from natural sources, and the C_9 acid (11) was obtained by oxydative degradation of ricinoleic acid. The configuration of the members with 4, 5, 6 (see *Chart 1*), and 10 (12) carbon atoms was determined by chemical methods, tentative assignments having been made for others (10, 12, 13).

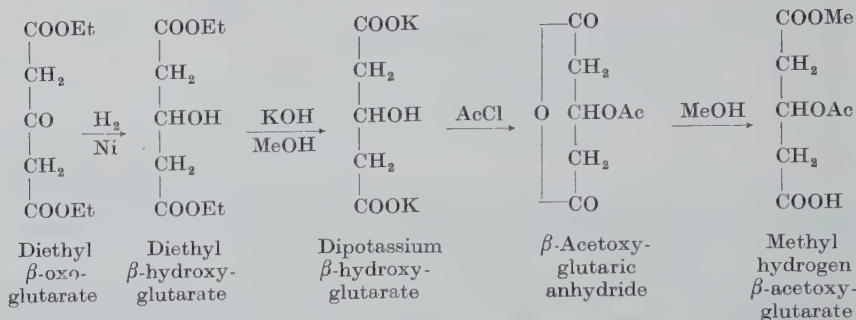
The complete series of racemic normal β -hydroxy acids up to and including the C_{24} acid is known (cf. 14, 15). Resolution by means of optically active bases has been effected in the case of the C_4 (cf. 16) and C_{14} (10) members, but was tried without success on the C_9 (11) and C_{12} (17) acids.

As it is impossible to foresee with certainty whether or not resolutions not previously attempted will meet with success, the use of a small optically active hydroxy-compound in chain-lengthening syntheses is of more general application. This method has already been employed in the synthesis of optically active 2-hydroxyalkanes (18, 19) and α -hydroxy acids (20). In both cases were products of known configuration obtained, because the carbon chain of key intermediates of known configuration was lengthened without interference with the asymmetric centre.

As already pointed out in Part I (18) of this series, a derivative of β -hydroxyglutaric acid should be a suitable key substance for the synthesis of β -hydroxy acids. Preliminary experiments with racemic methyl hydrogen β -acetoxyglutarate showed that its carbon chain could easily be lengthened by the Kolbe (cf. 21, 22) electro-synthesis. The half-ester, which has not been described previously, was made by the following sequence of reactions:

¹ Parts I and II: refs. (18) and (19).

² A preliminary report on part of this work has been published (12).



The half-ester was obtained as a viscous liquid in an over-all yield of about 46 % (4 steps). Compared with β -acetoxybutanoic acid (cf. 18), methyl hydrogen β -acetoxyglutarate is fairly stable; in spite of its boiling-point being 50–60° higher at 0.5 mm, only slight decomposition was observed on rapid distillation at this pressure.

β -Acetoxy methyl esters resulting from anodic chain extension of the half-ester were submitted to alkaline hydrolysis, but only low yields of free β -hydroxy acids were obtained. This is now understandable in view of the work of Linstead, Owen, and Webb (23), who show that alkaline hydrolysis of β -acetoxy esters may give appreciable amounts of α,β -unsaturated acids. The desired transformation was achieved in good yield by acid-catalysed de-acetylation with methanol followed by alkaline hydrolysis of the resulting β -hydroxy ester.

Resolution of racemic methyl hydrogen β -acetoxyglutarate was effected by means of optically active bases. Recrystallization of the cinchonidine salt from ethyl acetate (+ ether) to constant rotation of the half-ester gave approximately 30 % of distilled product with the molecular rotation $[\text{M}]_{\text{D}}^{25} + 12.5^\circ \pm 0.2^\circ$ (20 % solution in chloroform). Partly resolved laevorotatory half-ester from filtrates of the cinchonidine salt was used to make the strychnine salt, which on recrystallization from chloroform-ether to constant rotation of the half-ester gave a distilled product with $[\text{M}]_{\text{D}}^{21} - 12.7^\circ$ in about 25 % yield.

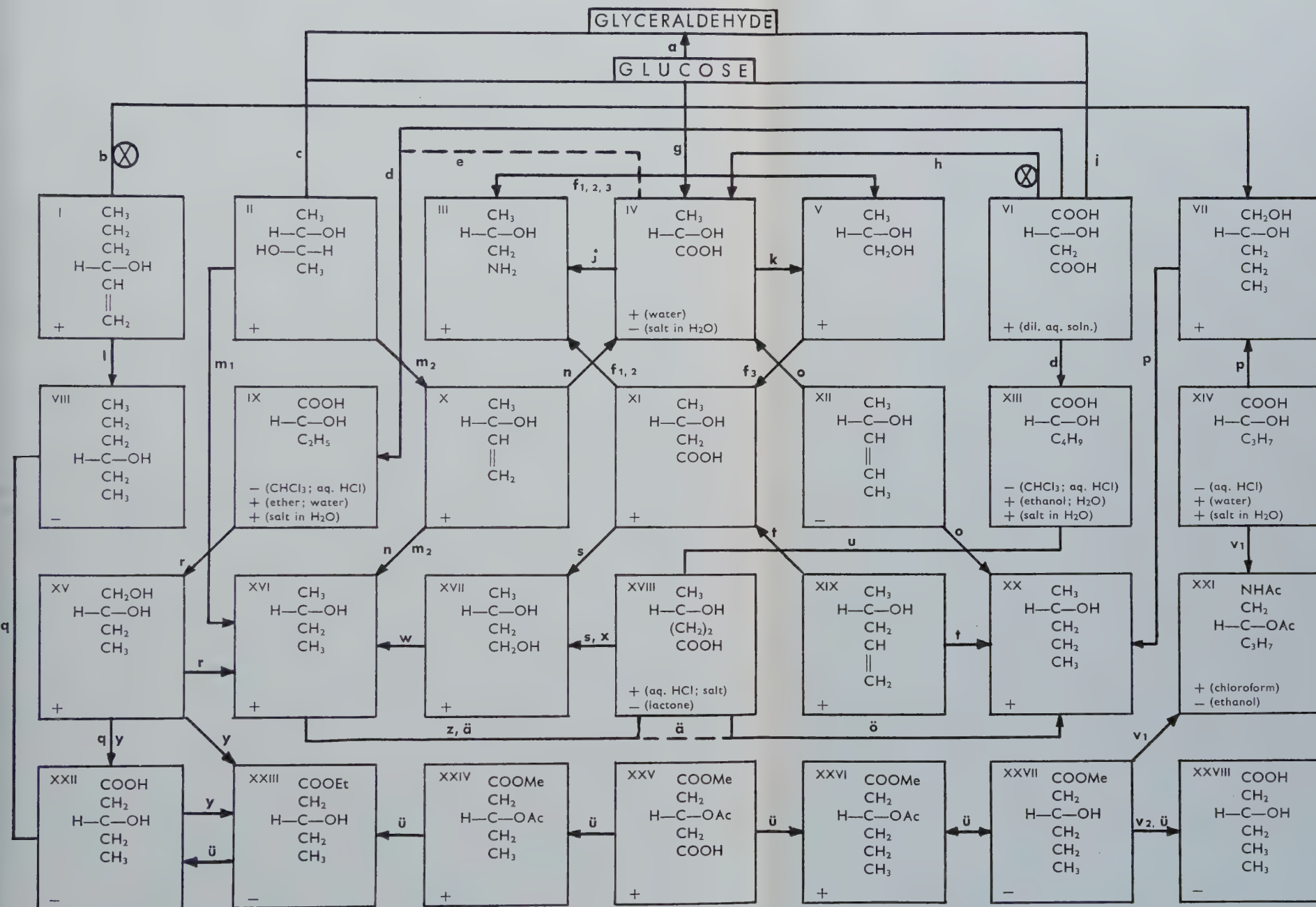
A check on the completeness of the resolution is provided by a comparison of the rotation of (–)-methyl β -hydroxyhexanoate, prepared from the dextrorotatory half-ester via the liquid acetoxy ester, with the rotation of (+)-methyl β -hydroxyhexanoate obtained by Lemieux (6) from ustilagic acid, a glucolipide produced by the corn smut *Ustilago zaeae*. The synthetic product, which was purified only by distillation, had within the limits of experimental error the same rotatory power as the natural product.

The constants here reported for the stereoisomers of methyl hydrogen β -acetoxyglutarate were measured on material subjected to one rapid distillation. The elemental analyses and molecular refractions are close to the theoretical values, but the rotatory power was found to decrease by 1.5 % (nearly twice the experimental error) on rapid re-distillation. In concordance with this finding, a decomposition of about 2 mole-% was calculated when the condensate in the cold trap was assumed to consist only of acetic acid. The figures for the rotatory power of completely resolved methyl hydrogen β -acetoxyglutarate given in this paper may therefore be a little low.

A marked solvent effect, shown by a fall in optical activity of about 40 %, was observed when dry ether was used instead of chloroform (20 % solutions). Variations

Chart 1. Configurational correlation of methyl hydrogen β -acetoxyglutarate with glyceraldehyde by chemical methods.

The formulae are written as Fischer projections.



The symbol $\text{---}\textcircled{\text{X}}\text{---}$ indicates formal inversion, i.e. the reaction actually gives the other antipode.



in temperature or concentration had little effect on the activity of chloroform solutions. When the temperature of a 75 % solution was raised from 15° to 50° C, or if the concentration was increased from 5 to 75 % (at room-temperature), a steady decrease in rotation, of about 10 % in all, was observed in both cases.

For characterization of the antipodes, the crystalline monoureides formally derived from symmetrical bis(*p*-dimethylaminophenyl)urea were prepared by means of bis-(*p*-dimethylaminophenyl)carbodiimide (cf. 24). The ureides melted at 142°, and had the molecular rotation $[\text{M}]_D^{22} \mp 77^\circ$ (5 % solutions in chloroform). The rotation is opposite in sign to that of the completely resolved half-ester from which the ureide was made and is six times as high.

The configuration of the antipodes of methyl hydrogen β -acetoxyglutarate relative to glyceraldehyde¹ was determined by two independent routes (see *Chart 1*). The essential steps were the anodic coupling of the dextrorotatory antipode (XXV) with acetic and propanoic acid, to give the acetylated methyl esters (XXIV and XXVI) of (-)-3D-hydroxypentanoic acid (XXII) and (-)-3D-hydroxyhexanoic acid (XXVIII), respectively. The results thus agree in showing that dextrorotatory methyl hydrogen β -acetoxyglutarate has the acetoxy group to the right in a Fischer projection formula (26, 27) written with the methyl ester group at the top. When the top carbon atom is numbered 1, the dextrorotatory antipode may be termed (+)-methyl 3D-acetoxy-4-carboxybutanoate. If the projection formula is turned through 180° in the plane of the paper, so that the free carboxyl group comes at the top, the acetoxy group will lie on the left; the dextrorotatory antipode may therefore equally well be termed (+)-3L-acetoxy-4-methoxycarbonylbutanoic acid. This way of naming optical isomers (cf. 18, 28) leads to unambiguous designations without the need for priority rules for top groups. In this paper the first name, with (-)-methyl 3L-acetoxy-4-carboxybutanoate for the laevorotatory antipode, is preferred, because the optically active β -hydroxy acids then receive the same configurational designation as the half-ester antipode from which they are made. In naming the monoureides, however, it is more convenient to regard the half-esters as derivatives of butanoic acid than of methyl butanoate.

By electrolysis of (+)-methyl hydrogen β -acetoxyglutarate in the presence of a large excess of acetic and propanoic acid, the "crossed" coupling products,² (+)-methyl β -acetoxy-pentanoate and (+)-methyl β -acetoxyhexanoate, respectively, were obtained in about 50 % yield (cf. 29).

The two acetoxy esters had closely similar molecular rotations, which were about twice as high in carbon disulphide solution as in methanol. Similar and even more pronounced solvent effects were observed in the case of the laevorotatory hydroxy esters obtained by acid-catalysed de-acetylation of the dextrorotatory acetoxy esters.

Acid-catalysed trans-esterifications of esters of simple saturated secondary aliphatic alcohols have been found to result in acyl-oxygen bond fission (30). Walden inversion or racemisation should therefore not occur in the above de-acetylation reactions. This was experimentally verified by re-acetylation of (-)-methyl β -hydroxyhexanoate with acetyl chloride. (+)-Methyl β -acetoxyhexanoate with the original rotatory power was obtained. Base-catalysed de-acetylation also proceeded without Walden inversion. This follows from the fact that laevorotatory

¹ Bijvoet *et al.* (cf. 25) have recently found by X-ray crystallography that the configuration of a substance relative to glyceraldehyde represents its true or absolute configuration.

² The symmetrical coupling products of the half-esters will be described at a later date.

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Names of compounds in Chart 1

- | | |
|----------------------------------|---|
| I. (+)-1-Hexen-3L-ol | XIV. 2D-Hydroxypentanoic acid |
| II. (+)-2D,3L-Butanediol | XV. (+)-1,2D-Butanediol |
| III. (+)-2L-Hydroxypropylamine | XVI. (+)-2D-Butanol |
| IV. (+)-2L-Hydroxypropanoic acid | XVII. (+)-1,3L-Butanediol |
| (+)-2L-Lactic acid ¹ | XVIII. (+)-4L-Hydroxypentanoic acid |
| V. (+)-1,2L-Propanediol | XIX. (+)-4-Penten-2D-ol |
| VI. (+)-2D-Hydroxysuccinic acid | XX. (+)-2D-Pentanol |
| (+)-2D-Malic acid ¹ | XXI. 1-Acetamido-2D-acetoxypentane |
| VII. (+)-1,2D-Pentenediol | XXII. (-)-3D-Hydroxypentanoic acid |
| VIII. (-)-3L-Hexanol | XXIII. (-)-Ethyl 3D-hydroxypentanoate |
| IX. 2D-Hydroxybutanoic acid | XXIV. (+)-Methyl 3D-acetoxypentanoate |
| X. (+)-3-Buten-2D-ol | XXV. (+)-Methyl 3D-acetoxy-4-carboxybutanoate |
| XI. (+)-3L-Hydroxybutanoic acid | XXVI. (+)-Methyl 3D-acetoxyhexanoate |
| XII. (-)-3-Penten-2D-ol | XXVII. (-)-Methyl 3D-hydroxyhexanoate |
| XIII. 2D-Hydroxyhexanoic acid | XXVIII. (-)-3D-Hydroxyhexanoic acid |

Chart 1 may be easier to survey by paying attention to the symmetrical positions occupied by the α -hydroxy acids IV, IX and XIII, by the 2-alkanols XVI and XX, by the alkenols X and XII, and by the α -, β - and γ -hydroxy acids IV, XI and XVIII, respectively. Furthermore, the compounds in the 1st and 3rd rows and in the 4th column are all dextrorotatory, and those in the 1st and 2nd, 6th and 7th columns are alternately dextro- and laevorotatory.

¹ Cf. G. E. McCasland's proposal in *A New General System for the Naming of Stereoisomers*. Pamphlet available from Chemical Abstracts, Ohio State University, Columbus 10, Ohio, U.S.A.

β -hydroxyhexanoic acid resulted when, in a preliminary experiment, the concentration of the sodium methoxide catalyst accidentally became so high that saponification occurred. This acid has been shown by Lemieux (6) to have a laevorotatory methyl ester.

(-)-3D-Hydroxyhexanoic acid was obtained as crystals melting at 42°. The racemic acid melts at 13° (14), but the melting-point for the optically active forms has not been reported previously. The rotatory power of the present sample was, with apposite sign, close to the figure given by Lemieux (6) for (+)-3L-hydroxyhexanoic acid obtained from ustilagic acid, and it was markedly higher in chloroform than in ethanol solution.

Partially resolved β -hydroxypentanoic acids were obtained by Levene and associates (31, 32) in the form of syrups. The racemic acid is reported to melt at 44° (14). The laevorotatory acid prepared in the course of this work was semi-solid, and melted completely at about 32°. Attempts to obtain it in crystalline form from solution were unsuccessful. It is known (3, 14) that short-chain β -hydroxy acids may be difficult to obtain in crystalline form. The rotatory power of the β -hydroxypentanoic acid was markedly higher in chloroform or ether than in ethanol or water solutions.

Lemieux and Giguere (13) have recorded the infra-red absorption spectrum of the hydrazide of optically active β -hydroxyhexanoic acid as a liquid-paraffin (Nujol) mull. For comparison the same compound was prepared from (-)-methyl β -hydroxyhexanoate of the present work, and the spectrum of a Nujol mull determined with a modified Hornig, Hyde, and Adcock (33) double-beam instrument.¹ Except for a strong, double absorption-peak between 6.0 and 6.2 μ , where the spectrum of Lemieux *et al.* has a strong single peak, no striking differences between the spectra were seen. Dr. Lemieux kindly supplied a sample of his laevorotatory hydrazide for comparison, and it was found that in the instrument of this Institute his sample also gave rise to the double peak (corresponding to C:O stretching and probably NH₂ bending vibrations). The spectrum of the hydrazide in a pressed potassium bromide disk and the spectra of a Nujol mull and of a chloroform solution in the 6 μ region are reproduced in *Figure 1*. The spectrum of the hydrazide in potassium bromide was checked in the 6 μ region with a Perkin-Elmer Model 21 spectrophotometer.

Experimental part²

Diethyl β -hydroxyglutarate

Attempts to prepare this compound from commercial 1,3-dichloro-2-propanol by nitrile synthesis gave yields much lower than reported (37). It was instead obtained by catalytic hydrogenation (38–42) of diethyl β -oxoglutarate (acetonedicarboxylate), made from citric acid by the simplified method of Baker *et al.* (43). (The oxo ester is also commercially available.)

To 404 g (2 moles) of diethyl β -oxoglutarate in a rocking steel-bomb was added 120 ml of a slurry of Raney nickel in 95 % ethanol. With an initial hydrogen pressure

¹ Built by Dr. M. Skogh of this Institute.

² Boiling-points uncorrected, melting-points corrected. When melting-points are given as an interval, they have been carefully determined with calibrated Anschütz thermometers as described in (34). Those given by a single figure have been determined on a Kofler bench (35).

$$\Delta n_D = (n_D^{30} - n_D^{15})/15.$$

The figure in parenthesis following the value for R_D is the molecular refraction calculated from the bond refractions of Vogel *et al.* (36).

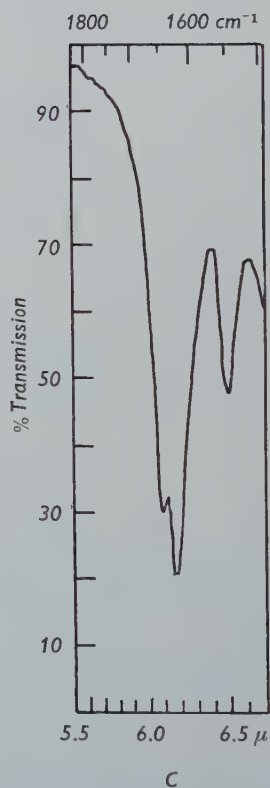
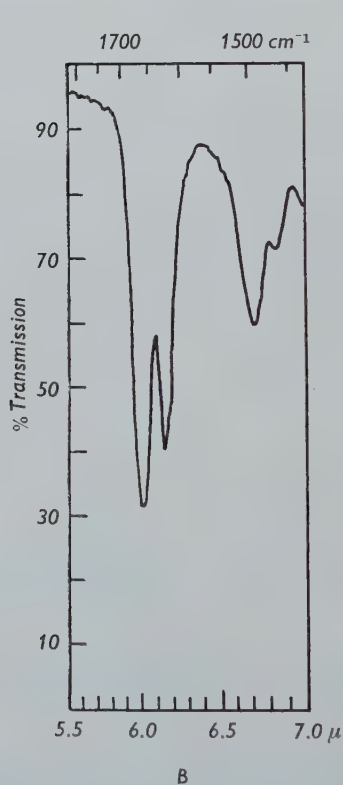
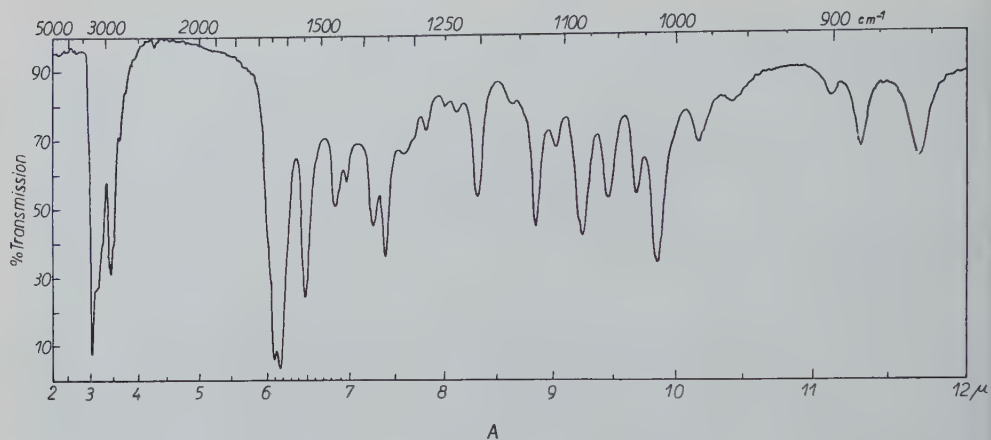


Fig. 1. Infra-red absorption spectra of (-)-3D-hydroxyhexanhydrazide. A. 0.8 mg of hydrazide in 300 mg of potassium bromide pressed to a circular disk 12 mm in diameter. B. 52 mg of hydrazide in 10 g of a chloroform solution (nearly saturated); 0.5 mm cell. C. Liquid-paraffin (Nujol) mull.

of 140 atm (at room-temperature), the reduction took from 1 to 5 hours at 100° C. The yield of distilled diethyl β -hydroxyglutarate (M 204.2) was 364 g (89%); b.p. 138–142°/10 mm (105–115°/1 mm), n_D^{20} 1.4392, $\Delta n_D - 0.00041$, d_4^{20} 1.103, R_D 48.72 (48.60). Reported n_D^{20} 1.4381 (38), n_D^{25} 1.4371, d_4^{25} 1.0814 (44).

Crude dipotassium β -hydroxyglutarate

To 102 g (0.5 mole) of diethyl β -hydroxyglutarate was added 67 g of KOH pellets followed by 200 ml of methanol, and the mixture distilled to dryness in half an hour on a boiling water-bath. Still on the bath the crude yellow salt was dried at 10 and finally 1 mm. and kept protected from moisture for use in the next step without further purification.

β -Acetoxyglutaric anhydride

This compound was first described by Blaise (45), who obtained it from β -hydroxyglutaric acid and acetyl chloride. Data on yields are lacking (46). In the present case dipotassium β -hydroxyglutarate was used instead of free acid, because the salt is easier to isolate. The yield of anhydride varied.

Dry crude dipotassium β -hydroxyglutarate from 0.5 mole of diethyl β -hydroxyglutarate was cooled to 0°, and 200 ml (nearly 3 moles) of acetyl chloride at 0° added. The temperature was allowed to rise to about 35° and was kept there for one hour. Excess acetyl chloride was distilled off from a water-bath kept at 70°, and the residue extracted with three portions of hot chloroform. When the filtered, deep red extract, concentrated under vacuum until the temperature of the vapour rose above 50° at 10 mm was cooled to room-temperature, the anhydride crystallized as light yellow plates, melting at 86°. A second crop of crystals was obtained by adding the wash-ether to the filtrate and cooling to 0°. The highest total yield was 56 g of anhydride pure enough for the next step (65% from diethyl β -hydroxyglutarate). If desired, the anhydride can be purified without great losses by crystallization at 0° from a few parts of acetic acid, acetyl chloride, or even ethanol, or by adding ether to its acetone, chloroform, or ethyl acetate solutions. Benzene or toluene (46) may also be used. Recrystallized, colourless β -acetoxyglutaric anhydride melted with slow decomposition except when finally crystallized from acetyl chloride. M.p. 86.2–86.9°; reported m.p. 87–88° (45), 87° (46).

Analysis:	49.0 % C	4.7 % H
$C_7H_5O_5$ (172.1):	48.84% C	4.68% H

Racemic methyl hydrogen β -acetoxyglutarate

This compound was initially made by dissolving pure β -acetoxyglutaric anhydride in about 10 parts of methanol and keeping the mixture at 35–40° overnight. Excess methanol was removed by suction, and the viscous residue dried over solid NaOH at 10 mm. When titrated with 1/10-normal NaOH using phenolphthalein as indicator, equivalent weights varying between 200 and 208 were found. This undistilled product was used in the preliminary resolution experiments. It was sparingly soluble in carbon disulphide, light petroleum, and toluene, but readily so in most other common

organic solvents. Attempts at crystallizing it from solutions cooled below -40° were unsuccessful. On one occasion a large amount of diester was formed by the preceding method, and the following procedure was adopted instead.

52 g (0.3 mole) of crude β -acetoxyglutaric anhydride was heated with 13 ml (7 % excess) of methanol for half an hour on a water-bath. The mixture was dissolved in 100 ml of water, and ammonia-water (1:2) added to the vigorously stirred solution through a dropping funnel kept with the stem in the mixture. The addition was stopped as soon as the smell of excess ammonia became perceptible. Some diester formed was extracted with ethyl acetate. The half-ester was isolated from the acidified solution by extraction with three portions of ethyl acetate, and the solvent removed under reduced pressure from the washed and dried¹ extract. Rapid vacuum distillation from a flask designed to minimize decomposition ("Kropfkolben", cf. (47)) gave 48 g of viscous *methyl hydrogen β -acetoxyglutarate* (79 % yield from the anhydride, 46 % from diethyl β -oxoglutarate); b.p. $145-155^{\circ}/0.5$ mm, n_D^{22} 1.4470, $\Delta n_D - 0.00034$, d_4^{22} 1.234, R_D 44.21 (44.15).

Analysis:	46.5 % C	6.0 % H		
$C_8H_{12}O_6$ (204.2):	47.06 % C	5.92 % H	$C_8H_{12}O_6 + 1.2 \% H_2O$:	46.49 % C 5.99 % H

Analysed at a later date the same sample gave figures corresponding to a water content of 2.5 %. Analysis of the optically active half esters gave correct results when precautions were taken to exclude moisture during their handling.

Resolution of methyl hydrogen β -acetoxyglutarate

Several alkaloids were tested for their ability to give readily crystallizing salts with the undistilled racemic half-ester. Aqueous solutions of the brucine, cinchonine, morphine, quinidine, and quinine salts gave on evaporation at room-temperature only glassy residues. Cinchonidine and strychnine, however, gave crystalline salts which were readily soluble in water and many of the common organic solvents, but relatively insoluble in ether.

The cinchonidine salt crystallized by addition of ether to its acetone, chloroform, or ethyl acetate, solutions. The half-ester isolated from the filtrates was laevorotatory in each case, and was most strongly so from ethyl acetate. This solvent was therefore adopted.

The strychnine salt crystallized by addition of ether to its chloroform solution. The half-ester isolated from the filtrate was laevorotatory in one case and dextro-rotatory in another. When, however, partly resolved laevorotatory half-ester from filtrates of the cinchonidine salt was used to make the strychnine salt, the resolution proceeded smoothly in the desired direction.

(+)-Methyl hydrogen β -acetoxyglutarate (XXV) (+)-Methyl 3D-acetoxy-4-carboxybutanoate

41 g (0.2 mole) of distilled racemic half-ester was dissolved with 59 g (0.2 mole) of cinchonidine in 300 ml of warm ethyl acetate, and 300 ml of ether added to the solution. The salt crystallizing at 0° was recrystallized from three parts of ethyl

¹ Sodium sulphate was used throughout this work.

acetate to which was added decreasing amounts of ether. The salt became less soluble in ethyl acetate as its purity increased, and no addition of ether was necessary in the final crystallizations. To follow the resolution, each filtrate was extracted with three portions of water, and the half-ester isolated from the acidified aqueous phases by extraction with three portions of ethyl acetate. The solvent was removed by suction, and the residue dried for 10 minutes at 100°C and 10 mm. Because of the high viscosity of the half-ester, the rotatory power of the resulting samples was measured in solution. About four recrystallizations were needed to give an undistilled half-ester of constant rotation¹ ($[\alpha]_D^{25} + 5.8^\circ$ (chloroform, *c* 20, *l* 1), n_D^{25} 1.445). The yield of nicely crystalline salt (soft needles in rosettes) was approximately 18 g (36 %); m.p. 89°, $[\alpha]_D^{22} - 62.5^\circ \pm 0.4^\circ$ (chloroform, *c* 5, *l* 1); partly resolved salt had a higher negative rotation. The melting-point was diffuse in a capillary tube, but fairly sharp and reproducible on a Kofler bench (48). Isolation and determination of the rotatory power of the half-ester should be unnecessary until the above constants for the salt are reached.

18.0 g of optically pure salt was dissolved in excess dilute hydrochloric acid saturated with sodium sulphate, the solution extracted with six portions of ether, and the extract washed once with a saturated aqueous solution of Na₂SO₄. Rapid vacuum distillation of the extract residue (6.6 g) from a small Claisen flask gave 6.0 g of viscous (+)-*methyl hydrogen β-acetoxyglutarate* (29 % yield from the racemic half-ester); b.p. 140–150°/0.3 mm, n_D^{20} 1.4474, $\Delta n_D - 0.00034$, d_4^{20} 1.236, R_D 44.17 (44.15).

	$[\alpha]_D^{25}$	$[M]_D^{25}$	Solvent	<i>c</i>	<i>l</i>
	$+ 6.1^\circ \pm 0.1^\circ$	$+ 12.5^\circ \pm 0.2^\circ$	chloroform	20	1
	$+ 5.28^\circ \pm 0.03^\circ$	$+ 10.78^\circ \pm 0.06^\circ$	none	123	0.5
	$+ 3.7^\circ \pm 0.1^\circ$	$+ 7.6^\circ \pm 0.2^\circ$	dry ether	20	1
Analysis:	47.0 % C	6.0 % H			
C ₈ H ₁₂ O ₆ (204.2):	47.06 % C	5.92 % H			

Rapid re-distillation of 3.0 g gave a product with $[\alpha]_D^{23} + 5.20^\circ \pm 0.03^\circ$ (undiluted). The cold trap contained 0.02 g of a condensate smelling like acetic acid.

(–)-*Methyl hydrogen β-acetoxyglutarate*

(–)-*Methyl 3L-acetoxy-4-carboxybutanoate*,

43 g (0.21 mole) of distilled, partly resolved half-ester ($[\alpha]_D^{20} - 1.0^\circ$ (chloroform, *c* 20, *l* 1), thus containing 25 g (0.12 mole) of the laevorotatory antipode) was dissolved with 57 g (0.17 mole) of finely-powdered strychnine in 300 ml of warm chloroform, and 300 ml of ether added to the solution. The salt crystallizing at room-temperature was recrystallized from chloroform by adding an equal volume of ether. To follow the resolution, the strychnine was precipitated from the mother liquours with ammonia–water, and the half-esters were isolated from the acidified filtrates as described in the case of the cinchonidine salt. As tests had shown that the rotatory power of the half-ester may diminish in ammonia solution, precautions were taken to avoid using a large excess, and to filter off the alkaloid and acidify the filtrate as quickly as possible. About five recrystallizations were needed to give an undistilled half-ester of constant rotation ($[\alpha]_D^{20} - 5.9^\circ$ (chloroform, *c* 20, *l* 1); n_D^{25} 1.445). The

¹ Optical rotations were measured with polarimeters of the Lippich triple-field type. The angles could usually be read to $\pm 0.01^\circ$.

yield of crystals (which looked much like those of the cinchonidine salt) was approximately 23 g (35 %); m.p. 70° (unsharp); $[\alpha]_D^{22} - 31.3^\circ \pm 0.4^\circ$ (chloroform, *c* 5, *l* 1); partly resolved salt had a higher negative rotation.

Ether-extracted half-ester (6.9 g) from 23.0 g of optically pure strychnine salt gave, on rapid distillation at 0.2 mm, 6.2 g of (-)-methyl hydrogen β -acetoxyglutarate (25 % of the amount present in the partly resolved half-ester used for making the strychnine salt); n_D^{25} 1.4450, $\Delta n_D - 0.00033$; d_4^{25} 1.231; R_D 44.14 (44.15).

$[\alpha]_D^{21}$	$[M]_D^{21}$	Solvent	<i>c</i>	<i>l</i>
$-6.2^\circ \pm 0.1^\circ$	$-12.7^\circ \pm 0.2^\circ$	chloroform	20	1
$-5.27^\circ \pm 0.05^\circ$	$-10.76^\circ \pm 0.1^\circ$	none	123	0.5
$-3.7^\circ \pm 0.1^\circ$	$-7.6^\circ \pm 0.2^\circ$	dry ether	20	1
Analysis:	47.1 % C	6.2 % H		
C ₈ H ₁₂ O ₆ (204.2):	47.06 % C	5.92 % H		

Characterization of the antipodes of methyl hydrogen β -acetoxyglutarate as the monoureides of symmetrical bis(*p*-dimethylaminophenyl)urea (49, 50)

To 0.31 g (1.5 millimoles) of distilled, completely resolved half-ester was added a clear solution of 0.42 g (1.5 millimoles) of bis(*p*-dimethylaminophenyl)carbodiimide¹ (51) in 30 ml of ether, and the mixture refluxed for three hours. Cooling to 0° gave about 0.58 g (80 % yield) of yellow crystals. After treatment with activated carbon in chloroform solution and crystallization from the same solvent by addition of ether, shiny, yellowish plates melting at 142° were obtained. Slow decomposition seemed to occur at the melting-point, as crystals kept near to this for some time melted at a lower temperature.

The dextrorotatory half-ester gave (-)-1-(3*l*-acetoxy-4-methoxycarbonylbutanoyl)-1,3-bis(*p*-dimethylaminophenyl)urea with $[\alpha]_D^{23} - 15.7^\circ \pm 0.4^\circ$ (chloroform, *c* 5, *l* 1), $[M]_D^{23} - 76.1^\circ \pm 1.9^\circ$.

The laevorotatory half-ester gave (+)-1-(3*D*-acetoxy-4-methoxycarbonylbutanoyl)-1,3-bis(*p*-dimethylaminophenyl)urea with $[\alpha]_D^{21} + 16.0^\circ \pm 0.4^\circ$ (chloroform, *c* 5, *l* 1), $[M]_D^{21} + 77.5^\circ \pm 1.9^\circ$.

Analysis:	(-)-ureide:	11.1 % N
	(+)-ureide:	11.3 % N
C ₂₅ H ₃₂ O ₆ N ₄ (484.5):		11.56 % N

(+)-Methyl 3*D*-acetoxyhexanoate (XXVI)

*By electrolysis*²: To 6.0 g (0.03 mole) of undistilled, completely resolved (+)-methyl hydrogen β -acetoxyglutarate ($[\alpha]_D^{23} + 5.8^\circ$ (chloroform, *c* 20, *l* 1), n_D^{25} 1.445) in 12.6 g (0.17 mole) of propanoic acid was added a solution of 0.1 g of sodium in 40 ml of methanol, and the mixture electrolysed at about 50 volts, with external water-cooling. When after 3 hours the solution had become neutral (average current

¹ A gift from Professor F. L. Breusch, University of Istanbul, Turkey, to Professor E. Stenhagen.

² The electrolyses were run with three smooth platinum-sheet electrodes (25 × 20 × 1 mm) mounted 2 mm apart in a bakelite frame.

ca. 2 amperes, 90 % current-yield), 100 ml of water was added and the mixture extracted with five portions of light petroleum.¹ The extract residue was boiled for 15 minutes with excess acetyl chloride (to acetylate any de-acetylated material), and washed in ether solution, firstly with a saturated aqueous solution of NaHCO_3 and then with water. Vacuum distillation² of the dried product gave 2.9 g of (+)-methyl β -acetoxyhexanoate (52 % yield); b.p. $50-60^\circ/0.5$ mm, n_D^{23} 1.4218, Δn_D -0.00040 , d_4^{23} 1.018, R_D 46.96 (47.24).

$[\alpha]_D^{22}$	$[M]_D^{22}$	Solvent	<i>c</i>	<i>l</i>
$+10.7^\circ \pm 0.4^\circ$	$+20.1^\circ \pm 0.8^\circ$	carbon disulphide	5	1
$+9.6^\circ \pm 0.4^\circ$	$+18.1^\circ \pm 0.8^\circ$	chloroform	5	1
$+9.21^\circ \pm 0.04^\circ$	$+17.34^\circ \pm 0.08^\circ$	none	102	1
$+4.9^\circ \pm 0.4^\circ$	$+9.2^\circ \pm 0.8^\circ$	methanol	5	1

By re-acetylation: 0.25 g of (-)-methyl β -hydroxyhexanoate (from the following experiment) was boiled for 15 minutes with excess acetyl chloride, and the resulting product washed, in ether solution, firstly with a saturated aqueous solution of NaHCO_3 and then with water. Distillation of the dried product at 0.5 mm gave 0.23 g of (+)-methyl β -acetoxyhexanoate (92 % yield); n_D^{21} 1.4227, d_4^{21} 1.016, R_D 47.15 (47.24), $[\alpha]_D^{21} +9.6^\circ \pm 0.4^\circ$ (chloroform, *c* 5, *l* 1). The density is somewhat lower than that of the sample above, giving a molecular refraction closer to the theoretical value.

Analysis:	57.8 % C	8.6 % H
$\text{C}_9\text{H}_{16}\text{O}_4$ (188.2):	57.43 % C	8.57 % H

(-)-Methyl 3D-hydroxyhexanoate (XXVII)

To 1.9 g (0.01 mole) of optically pure (+)-methyl β -acetoxyhexanoate was added 100 ml of methanol containing 2 ml of concentrated hydrochloric acid (*d* 1.19), and the mixture concentrated to 20-30 ml by distillation at ordinary pressure over a period of about half an hour. This procedure was repeated with two further portions of methanol (100 ml) containing 1 and 0 ml of acid, respectively. 100 ml of ether was then added, and the solution washed once with saturated aqueous NaHCO_3 and twice with a little water. Vacuum distillation gave 1.1 g of (-)-methyl β -hydroxyhexanoate (*M* 146.2, 75 % yield); b.p. $80-82^\circ/8$ mm, n_D^{23} 1.4281, Δn_D -0.00040 , d_4^{23} 0.999, R_D 37.65 (37.71).

$[\alpha]_D^{23}$	$[M]_D^{23}$	Solvent	<i>c</i>	<i>l</i>
$-37.7^\circ \pm 0.4^\circ$	$-55.1^\circ \pm 0.6^\circ$	carbon disulphide	5	1
$-26^\circ \pm 2^\circ$	$-38^\circ \pm 3^\circ$	chloroform	1	1
$-24.9^\circ \pm 0.4^\circ$	$-36.4^\circ \pm 0.6^\circ$	„	5	1
$-9.7^\circ \pm 0.1^\circ$	$-14.2^\circ \pm 0.1^\circ$	none	100	0.2
$-7.1^\circ \pm 0.4^\circ$	$-10.4^\circ \pm 0.6^\circ$	methanol	5	1

Lemieux *et al.* give $[\alpha]_D +28^\circ$ (chloroform, *c* 0.86, *l* 2) for a sample with n_D^{25} 1.427 obtained from ustilagic acid (6); and $[\alpha]_D -27.1^\circ$ (chloroform, *c* 1, *l* 2) for a sample with n_D^{23} 1.422 (?), obtained by reduction of sodium β -oxohexanoate with fermenting yeast followed by esterification with diazomethane (13).

¹ The boiling-range of the light petroleum used throughout this work was $40-60^\circ$.

² This and the following distillations were done through a small Vigreux column (5×1 cm).

(-)-3D-Hydroxyhexanhydrazide

This compound was prepared from (-)-methyl β -hydroxyhexanoate and hydrazine by the general procedure of Sah (52). After crystallization from a large amount of ether the hydrazide (M 146.2) was obtained as soft silky needles melting at 130° .

$[\alpha]_D^{22}$	$[M]_D^{22}$	Solvent	c	l
$-15^\circ \pm 2^\circ$	$-22^\circ \pm 3^\circ$	water	1	1
$-38^\circ \pm 6^\circ$	$-56^\circ \pm 9^\circ$	chloroform	0.5	1

Lemieux *et al.* give m.p. 130 – 131° , $[\alpha]_D +15.9^\circ$ (water, c 0.75, l 2) (6) and m.p. 131 – 132° , $[\alpha]_D -15.6^\circ$ (water, c 0.9, l 2) (13).

(-)-3D-Hydroxyhexanoic acid (XXVIII)

In an attempt to de-acetylate (+)-methyl β -acetoxyhexanoate (0.54 g, $[\alpha]_D^{21} +8.6^\circ$ (undiluted), i.e. 94 % optically pure) by methanol using sodium methoxide as catalyst, the concentration of catalyst was too high, and saponification occurred. The acid fraction (0.25 g), which was isolated by extraction with ethyl acetate and distilled at 1 mm (b.p. *ca.* 60°) gave after two crystallizations from light petroleum transparent plates (0.05 g) of (-)- β -hydroxyhexanoic acid (M 132.2).

$[\alpha]_D^{24}$	$[M]_D^{24}$	Solvent	c	l
$-28^\circ \pm 1^\circ$	$-37^\circ \pm 1^\circ$	chloroform	2	1
$-1^\circ \pm 1^\circ$	$-1^\circ \pm 1^\circ$	ethanol	2	1

After one more crystallization from light petroleum, the acid melted at 41 – 41.6° .

For an impure sample of the antipode obtained from ustilagic acid Lemieux (6) reports $[\alpha]_D +30^\circ$ (chloroform, c 2, l 2).

(+)-Methyl 3D-acetoxypentanoate (XXIV)

To 5.3 g (0.026 mole) of distilled, completely resolved (+)-methyl hydrogen β -acetoxyglutarate in 15 ml (0.26 mole) of acetic acid was added a solution of 0.1 g of sodium in 50 ml of methanol, and the mixture electrolysed at about 40 volts without cooling. The solution became neutral after 5 hours and 45 minutes (average current *ca.* 1.5 amperes, 89 % current-yield), and the reaction product was isolated as described in the case of the next higher homologue. Distillation gave 2.24 g of (+)-methyl β -acetoxy-pentanoate (50 % yield); b.p. 74 – $76^\circ/5$ mm, n_D^{20} 1.4200, $\Delta n_D -0.00041$, d_4^{20} 1.039, R_D 42.43 (42.59).

$[\alpha]_D^{21}$	$[M]_D^{21}$	Solvent	c	l
$+12.2^\circ \pm 0.4^\circ$	$+21.3^\circ \pm 0.7^\circ$	carbon disulphide	5	1
$+9.8^\circ \pm 0.4^\circ$	$+17.1^\circ \pm 0.7^\circ$	chloroform	5	1
$+8.07^\circ \pm 0.04^\circ$	$+14.06^\circ \pm 0.07^\circ$	none	104	0.5
$+5.2^\circ \pm 0.4^\circ$	$+9.1^\circ \pm 0.7^\circ$	methanol	5	1

Analysis:	55.4 % C	8.1 % H
$C_8H_{14}O_4$ (174.2):	55.16 % C	8.10 % H

(-)-Ethyl 3D-hydroxypentanoate (XXIII)

1.9 g of (+)-methyl β -acetoxy-pentanoate was de-acetylated in the same way as the next higher homologue, except that ethanol was used instead of methanol. By distillation of the resulting product, fractions with specific rotations from -10 to 0° (undiluted substance) were obtained. The de-acetylation had apparently been incomplete, and the product was therefore submitted to the same treatment once more. This time distillation gave fractions with the same rotatory power. The final yield was 0.5 g of (-)-ethyl β -hydroxypentanoate (M 146.2; b.p. $92-93^\circ/15$ mm, n_D^{25} 1.4235, $\Delta n_D - 0.00037$, d_4^{25} 0.990, R_D 37.64 (37.71).

$[\alpha]_D^{25}$	$[M]_D^{25}$	Solvent	c	l
$-38.3^\circ \pm 0.4^\circ$	$-56.0^\circ \pm 0.6^\circ$	carbon disulphide	5	1
$-31.4^\circ \pm 0.4^\circ$	$-45.9^\circ \pm 0.6^\circ$	chloroform	5	1
$-14.7^\circ \pm 0.1^\circ$	$-21.5^\circ \pm 0.1^\circ$	none	99	0.2
$-14.2^\circ \pm 0.4^\circ$	$-20.8^\circ \pm 0.6^\circ$	methanol	5	1

The highest value reported (32) for the rotation of undiluted ester is $\alpha_D^{20} - 10.63^\circ$ (l 1), but the sample was not claimed to be optically pure. It had been made by acid-catalysed esterification of an acid derived from dextrorotatory 1,2-butanediol (see next paragraph).

(-)-3D-Hydroxypentanoic acid (XXII)

0.27 g of (-)-ethyl β -hydroxypentanoate was dissolved in 10 ml of a 10 % aqueous solution of KOH and the mixture left overnight after dilution with 40 ml of water. The alkaline solution was then extracted with three portions of ether, acidified, and after saturation with ether-washed Na_2SO_4 , was extracted with five portions of freshly distilled ether. The extract, washed twice with a small portion of a saturated aqueous solution of Na_2SO_4 and dried, gave on evaporation 0.19 g of viscous crude acid. Distillation at 5 mm (b.p. *ca.* 100°) gave semi-solid (-)- β -hydroxypentanoic acid (M 118.1) which melted completely at about 32° . Attempts at crystallizing the acid from light petroleum containing a little ether were unsuccessful.

$[\alpha]_D^{25}$	$[M]_D^{25}$	Solvent	c	l
$-35^\circ \pm 1^\circ$	$-41^\circ \pm 1^\circ$	chloroform	2	1
$-28^\circ \pm 1^\circ$	$-33^\circ \pm 1^\circ$	ether	2	1
$-14^\circ \pm 1^\circ$	$-17^\circ \pm 1^\circ$	water	2	1
$-11^\circ \pm 1^\circ$	$-13^\circ \pm 1^\circ$	ethanol	2	1

The highest rotatory power reported for β -hydroxypentanoic acid is $[\alpha]_D^{23} - 15.2^\circ$ (c 3.28, l 2), $[M]_D^{23} - 17.9^\circ$, found by Levene and Haller (31) when an excess of 1-normal HCl was added to an aqueous solution of the sodium salt (with $[\alpha]_D^{23} - 9.3^\circ$ (water, c 6.47, l 1)). For another sample Levene and Mori (32) found $[\alpha]_D^{20} - 10^\circ$ in ether. None of the samples was claimed to be optically pure. They had been made by nitrile synthesis from dextrorotatory 1,2-butanediol obtained from 2-oxobutanol by reduction with fermenting yeast.

Summary

Racemic methyl hydrogen β -acetoxyglutarate was synthesized via β -acetoxyglutaric anhydride and completely resolved by fractional crystallization of the cinchonidine and strychnine salts. The configuration of the antipodes relative to glyceraldehyde was determined by the synthesis of $(-)$ -3D-hydroxypentanoic and $(-)$ -3D-hydroxyhexanoic acid from the dextrorotatory half-ester, making use of the Kolbe anodic synthesis. The optically active β -hydroxyhexanoic acid was obtained in crystalline form, m.p. 42° .

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On the thermodynamics of ion exchange equilibria

I. The thermodynamical equilibrium equation in relation to reference states and components

By LENNART W. HOLM

Introduction

The equilibrium between an ion exchanging substance and a surrounding electrolyte solution has been treated by many authors. Several thermodynamical relationships have been proposed, some by considering the ion exchange equilibrium as a Donnan equilibrium and some by treating it as a reaction equilibrium using the law of mass action. The thermodynamical equivalence of these formally different treatments does not seem, however, to have been realized by some authors. The main aim of this paper is to point out this equivalence by the derivation of the different equilibrium equations from one general equation. This general equation will be obtained by considering the ion exchange equilibrium as a Gibbs-Donnan equilibrium.

The equilibrium between two solutions separated by a membrane is, if the membrane prevents one or more electrically charged components from being freely distributed between the two solutions, usually called a Gibbs-Donnan equilibrium. This is after Donnan, who made the first, though approximative, thermodynamic treatment [1]. The mechanism by which restriction of movement of a charged component occurs is of course without importance from the thermodynamical point of view, i.e. the presence of certain restrictions in the free diffusion of one or more electrically charged components is the only condition for considering an equilibrium as a Gibbs-Donnan equilibrium [2]. This condition is completely fulfilled in ion exchange equilibria, where the pertinent charged component is the ion exchange polymer, the insolubility of which prevents it from moving freely. Thus there is no reason for doubting the correctness in treating the equilibrium between an ion exchanger with its counter ions and a surrounding electrolyte solution as a Gibbs-Donnan equilibrium. The initiation of an advanced application of the Gibbs-Donnan equilibrium to ion exchange equilibria was provided by Gregor [3, 4] and resulted in quite a number of publications from different quarters. Unfortunately, as one of his successors puts it, "... the interpretation of his paper is obscured by ambiguities concerning ... the meaning of his activity coefficients, which are not defined" [5]. This situation has resulted in

misunderstanding¹ and moreover the objection is more or less also true for some of Gregor's successors.

In consequence of what has just been said, it seems justifiable to deduce the formally different equations which are obtained for different choices of reference states. For the same reason the functional dependences of the quantities entering these deductions are written out in full despite the resulting prolixity.

List of symbols used in this paper

α_A	Activity of component A .
F	Faraday constant.
f_{AR}	Rational activity coefficient of component AR .
K	Thermodynamical equilibrium constant.
K_m	Selectivity coefficient (equilibrium ratio in molalities).
m_A	Molality of component A .
N_{AR}	Equivalent fraction in ion exchanger phase of component AR .
n_w	Number of moles of water per equivalent ion exchanger.
n_A	Number of moles of water per equivalent ion exchanger completely saturated with ion A .
p	External pressure.
R	Gas constant.
T	Absolute temperature.
V_A	Volume of one equivalent ion exchanger completely saturated with ion A .
v_A	Partial molal volume of component A .
z_A	Valence of ion A .
γ_A	Molal activity coefficient of component A .
α	Equilibrium ratio. (Ion exchanger phase: Equivalent fractions; Solution phase: Activity coefficients included.)
μ_A	Chemical potential of component A .
$\bar{\mu}_i$	Electrochemical potential of ion i .
ν_+, ν_-	Numbers of cations and anions, respectively, produced by dissociation of one molecule of electrolyte.
ν	$= \nu_+ + \nu_-$.
ν_A, ν_X	Numbers of A and X ions respectively, produced by dissociation of one molecule of the electrolyte $A_{\nu_A} X_{\nu_X}$.
τ	Molar volume of water vapor.
ψ	Electrical potential.

Superscript ' indicates a quantity in phase '.

Superscript '' indicates a quantity in phase ''.

Superscript ⁰ indicates that the quantity refers to the standard state.

Subscripts r_A or r_B indicate that the quantity refers to the reference state of A or B respectively.

Underlining means that the quantity is constant.

The reference state is given within square brackets [] after affected properties. The actual state is given within round brackets () after affected properties.

¹ Apparently a mistake of this kind is the reason for Marinsky's criticism [6] of Gregor's equilibrium equation.

Equilibrium equations for different reference states

In a Gibbs-Donnan equilibrium between a solution and pure solvent separated by a semipermeable membrane, the osmotic pressure of the solution is that pressure which has to be applied on the solution to maintain the equilibrium, i.e. to prevent the diffusion of solvent into the solution. To preserve an equilibrium between two solutions of different compositions, there must consequently be applied to one of the solutions an external pressure equal to the difference between the osmotic pressures of the solutions. In the classical illustration of osmotic pressure this pressure difference is brought about by means of a water column. In ion exchangers, however, the osmotic pressure difference is compensated by the so called swelling pressure of the ion exchanger polymer. Thus a Gibbs-Donnan equilibrium is principally an equilibrium between two electrolyte solutions of different compositions and under different pressures. The following deductions are quite general but the discussion of certain special cases will be limited to ion exchange equilibria.

The distribution of an electrically charged component, e.g. the ion i between the phase ' and the phase ' ', is determined by the condition that the electrochemical potential $\bar{\mu}_i$ of the stated component must be the same in both phases at equilibrium:

$$\bar{\mu}_i'(p', m_1', m_2', \dots) = \bar{\mu}_i''(p'', m_1'', m_2'', \dots). \quad (1)$$

$\bar{\mu}_i$ depends on the pressure, p , in the phase and on the composition of the phase m_1, m_2 etc. and in addition of course on the temperature. The last-mentioned parameter is, however, the same in both phases and is assumed to be constant; consequently mentioning and denoting the temperature dependence has been abandoned throughout. To avoid complications, the composition has to be expressed in units independent of pressure, i.e. not in for example (volume) molarity but in per cent by weight, molality or mole fraction. Here molality has been chosen but the equations are of course also valid for other pressure independent concentration units provided that the respective quantities are given the appropriate values.

According to the definition we have:

$$\bar{\mu}_i = \mu_i + z_i F \psi \quad (2)$$

where μ_i is the chemical potential of the ion i , z_i its charge, F the Faraday constant and ψ the electric potential of the phase. From eqns. (1) and (2) we obtain the equilibrium condition:

$$\mu_i' = \mu_i'' + z_i F (\psi'' - \psi'). \quad (3)$$

For an uncharged substance u , e.g. the solvent, the equilibrium condition may be regarded as a special case of eqn. (3) since $z_u = 0$:

$$\mu_u' = \mu_u'' \quad (4)$$

The electric potentials will be cancelled when forming the equation for the distribution equilibrium of two diffusible, charged species between the two phases.

Table 1.

Phase ' (external solution)	Phase '' (ion exchanger)
EQUILIBRIUM STATE	
p'	p'' pressure
ψ'	ψ'' electric potential
m'_A	m''_A concentration of ion A
m'_B	m''_B concentration of ion B
$\mu'_A(p', m'_A, m'_B)$	$\mu''_A(p'', m''_A, m''_B)$ chemical potential of ion A
$\mu'_B(p', m'_A, m'_B)$	$\mu''_B(p'', m''_A, m''_B)$ chemical potential of ion B
$\gamma'_A[p'_{r_A}, (m'_A, m'_B)_{r_A}](p', m'_A, m'_B)$	$\gamma''_A[p''_{r_A}, (m''_A, m''_B)_{r_A}](p'', m''_A, m''_B)$ activity coefficient of ion A
$\gamma'_B[p'_{r_B}, (m'_A, m'_B)_{r_B}](p', m'_A, m'_B)$	$\gamma''_B[p''_{r_B}, (m''_A, m''_B)_{r_B}](p'', m''_A, m''_B)$ activity coefficient of ion B
REFERENCE STATES	
(states in which the activity coefficients are equal to unity)	
p'_{r_A}	p''_{r_A} pressure
$(m'_A, m'_B)_{r_A}$ ION A	$(m''_A, m''_B)_{r_A}$ composition
p'_{r_B}	p''_{r_B} pressure
$(m'_A, m'_B)_{r_B}$ ION B	$(m''_A, m''_B)_{r_B}$ composition

For simplicity we therefore consider the chemical potentials when studying the pressure dependence. Generally, we have:

$$\mu = \mu^0 + RT \ln a = \mu^0 + RT \ln m + RT \ln \gamma \quad (5)$$

where μ^0 is the chemical potential in the standard state, i.e. when the activity $a=1$, m the molality and γ the corresponding activity coefficient. It should perhaps be emphasized that, in connection with electrolyte solutions, often no real signification is attached to the standard state; instead μ^0 is chosen to make the activity coefficient $\gamma \rightarrow 1$ at a certain composition. In the following this certain composition is called the reference state [7] and denoted by the subscript r . An infinitely dilute solution is often taken as such a reference state. The chemical potential in the standard state as well as the activity coefficient are relative quantities and their absolute values depend on the choice of reference states. The reference state will further on be given within square brackets [] after affected quantities. We have of course e.g.

$$\mu'_A(p'_{r_A}, (m'_A, m'_B)_{r_A}) = \mu'^0_A[p'_{r_A}, (m'_A, m'_B)_{r_A}].$$

(This expression becomes, however, an identity if the reference state of i is a 1 molal solution.) This means that the chemical potential of the standard state, μ^0 , will not be identical with the chemical potential of the reference state, μ_r , and will thus not correspond to a real state, except when the reference state is a 1 molal solution. Instead, μ^0 may be considered as the chemical potential of an ideal (i.e. $\gamma=1$) 1 molal solution.

In order to simplify the notation somewhat, we consider the equilibrium of only two ions, A and B , between the phases ' and '. According to equation (5) we then have for the ion A in the phase ':

$$\begin{aligned}\mu'_A(p', m'_A, m'_B) &= \mu_A^0[p'_{r_A}, (m'_A, m'_B)_{r_A}] + RT \ln a'_A[p'_{r_A}, (m'_A, m'_B)_{r_A}](p', m'_A, m'_B) \\ &= \mu_A^0[p'_{r_A}, (m'_A, m'_B)_{r_A}] + RT \ln m'_A + RT \ln \gamma'_A[p'_{r_A}, (m'_A, m'_B)_{r_A}](p', m'_A, m'_B)\end{aligned}\quad (6)$$

where $\mu'_A(p', m'_A, m'_B)$ is the chemical potential of A in phase ' at the pressure p' and the composition m'_A, m'_B . The chemical potential of A in the standard state $\mu_A^0[p'_{r_A}, (m'_A, m'_B)_{r_A}]$ has been chosen to make the molal activity coefficient of the ion A $\gamma'_A[p'_{r_A}, (m'_A, m'_B)_{r_A}](p', m'_A, m'_B) \rightarrow 1$ when $p' \rightarrow p'_{r_A}$, $m'_A \rightarrow (m'_A)_{r_A}$, and $m'_B \rightarrow (m'_B)_{r_A}$. See also List of symbols, above, and Table 1, for further explanations of the symbols.

We shall assume that the composition of the reference state is constant; this we denote by $(\underline{m}'_A, \underline{m}'_B)_{r_A}$. The reference pressure may be either chosen constant $p'_{r_A} = p_{r_A} = \text{const.}$ or allowed to vary with the actual external pressure $p'_{r_A} = f(p')$.

An expression for the pressure dependence of the activity coefficient is obtained by partial derivation of eqn. (6) with respect to pressure:

$$\begin{aligned}RT \left(\frac{\partial \ln \gamma'_A[p'_{r_A}, (m'_A, m'_B)_{r_A}](p', m'_A, m'_B)}{\partial p'} \right)_{m'_A, m'_B} \\ = \left(\frac{\partial \mu'_A(p', m'_A, m'_B)}{\partial p'} \right)_{m'_A, m'_B} - \frac{\partial \mu_A^0[p'_{r_A}, (\underline{m}'_A, \underline{m}'_B)_{r_A}]}{\partial p'} \\ = v'_A(p', m'_A, m'_B) - v_A^0[p'_{r_A}, (\underline{m}'_A, \underline{m}'_B)_{r_A}] \frac{dp'_{r_A}}{dp'}\end{aligned}\quad (7)$$

where $v'_A(p', m'_A, m'_B)$ is the partial molal volume of A at the pressure p' and the composition m'_A, m'_B , and $v_A^0[p'_{r_A}, (\underline{m}'_A, \underline{m}'_B)_{r_A}]$ the partial molal volume in the standard state. The latter volume has a real meaning, even if the standard state has not, as is seen by applying eqn. (7) to the reference state, where $\gamma'_A = 1$ and thus $\ln \gamma'_A = 0$:

$$v_A^0[p'_{r_A}, (\underline{m}'_A, \underline{m}'_B)_{r_A}] = v'_A(p'_{r_A}, (m'_A, m'_B)_{r_A})\quad (8)$$

i.e. the partial molal volumes in standard and reference states are identical.

Equations analogous to eqns. (6), (7) and (8) are readily obtained for the ion A also in the phase '' and for B in both phases. A general equation for the

equilibrium of the ions A and B between the phases ' and '' is obtained by combination of eqns. (6) and (3) for the ion A with charge z_A and for the ion B with charge z_B respectively, and subsequent elimination of $(\psi'' - \psi')$:

$RT \ln$.

$$\begin{aligned} & \cdot \left\{ \frac{a'_A [p'_{rA}, (\underline{m}'_A, \underline{m}'_B)_{rA}] (p', m'_A, m'_B)}{a''_A [p''_{rA}, (\underline{m}''_A, \underline{m}''_B)_{rA}] (p'', m''_A, m''_B)} \right\}^{z_B} \cdot \left\{ \frac{a''_B [p''_{rB}, (\underline{m}''_A, \underline{m}''_B)_{rB}] (p'', m''_A, m''_B)}{a'_B [p'_{rB}, (\underline{m}'_A, \underline{m}'_B)_{rB}] (p', m'_A, m'_B)} \right\}^{z_A} \\ & = z_B \{ \mu_A''^0 [p''_{rA}, (\underline{m}''_A, \underline{m}''_B)_{rA}] - \mu_A'^0 [p'_{rA}, (\underline{m}'_A, \underline{m}'_B)_{rA}] \} - \\ & - z_A \{ \mu_B''^0 [p''_{rB}, (\underline{m}''_A, \underline{m}''_B)_{rB}] - \mu_B'^0 [p'_{rB}, (\underline{m}'_A, \underline{m}'_B)_{rB}] \}. \end{aligned} \quad (9)$$

Considering the choice of reference states, the following important special cases can be distinguished:

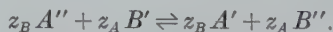
1. *The reference states are independent of pressure.* Each reference state is defined at a certain constant pressure; thus $\mu_A'^0 [p'_{rA}, (\underline{m}'_A, \underline{m}'_B)_{rA}] = \text{const.}$ etc. We obtain from eqn. (9)

$$\begin{aligned} & \left\{ \frac{a'_A [p'_{rA}, (\underline{m}'_A, \underline{m}'_B)_{rA}] (p', m'_A, m'_B)}{a''_A [p''_{rA}, (\underline{m}''_A, \underline{m}''_B)_{rA}] (p'', m''_A, m''_B)} \right\}^{z_B} \cdot \left\{ \frac{a''_B [p''_{rB}, (\underline{m}''_A, \underline{m}''_B)_{rB}] (p'', m''_A, m''_B)}{a'_B [p'_{rB}, (\underline{m}'_A, \underline{m}'_B)_{rB}] (p', m'_A, m'_B)} \right\}^{z_A} \\ & = \text{const.} = K \end{aligned} \quad (10)$$

where

$$\begin{aligned} RT \ln K = & z_B \{ \mu_A''^0 [p''_{rA}, (\underline{m}''_A, \underline{m}''_B)_{rA}] - \mu_A'^0 [p'_{rA}, (\underline{m}'_A, \underline{m}'_B)_{rA}] \} - \\ & - z_A \{ \mu_B''^0 [p''_{rB}, (\underline{m}''_A, \underline{m}''_B)_{rB}] - \mu_B'^0 [p'_{rB}, (\underline{m}'_A, \underline{m}'_B)_{rB}] \}. \end{aligned}$$

Equation (10) is of course identical with that equation which may be obtained by regarding the ion exchange equilibrium as the equilibrium state of a bimolecular, reversible reaction:



K is then the thermodynamical equilibrium constant for the reaction.

Introducing the selectivity (affinity or distribution) coefficient (sometimes wrongly called constant) K_m , which is very customary in connection with ion exchange:

$$K_m = \left(\frac{m'_A}{m''_A} \right)^{z_B} \cdot \left(\frac{m''_B}{m'_B} \right)^{z_A} \quad (11)$$

eqn. (10) may be written:

$$\begin{aligned} \ln K_m = & \ln K + \ln \frac{\{\gamma'_B [p'_{rB}, (\underline{m}'_A, \underline{m}'_B)_{rB}] (p', m'_A, m'_B)\}^{z_A}}{\{\gamma'_A [p'_{rA}, (\underline{m}'_A, \underline{m}'_B)_{rA}] (p', m'_A, m'_B)\}^{z_B}} - \\ & - \ln \frac{\{\gamma''_B [p''_{rB}, (\underline{m}''_A, \underline{m}''_B)_{rB}] (p'', m''_A, m''_B)\}^{z_A}}{\{\gamma''_A [p''_{rA}, (\underline{m}''_A, \underline{m}''_B)_{rA}] (p'', m''_A, m''_B)\}^{z_B}}. \end{aligned} \quad (12)$$

The activity coefficients are here dependent on the pressure, but since the pressures in the reference states are constant, i.e. independent of the actual pressure in the phase, the last term of eqn. (7) is zero; thus for γ'_A for example:

$$RT \left(\frac{\partial \ln \gamma'_A [\underline{p}'_{r_A}, (\underline{m}'_A, \underline{m}'_B)_{r_A}] (p', m'_A, m'_B)}{\partial p'} \right)_{m'_A, m'_B} = v'_A (p', m'_A, m'_B). \quad (13)$$

To eliminate the pressure dependence of the activity coefficients we introduce an activity coefficient $\gamma'_A [\underline{p}'_{r_A}, (\underline{m}'_A, \underline{m}'_B)_{r_A}] (p'_{r_A}, m'_A, m'_B)$. As before, this activity coefficient is defined at the actual composition of the solution but, also, at a constant pressure which is suitably chosen here to be equal to the pressure in the reference state, p'_{r_A} . The relation between this pressure-independent activity coefficient and the pressure-dependent one introduced earlier is obtained by integration of eqn. (13) from p'_{r_A} to p' :

$$RT \ln \gamma'_A [\underline{p}'_{r_A}, (\underline{m}'_A, \underline{m}'_B)_{r_A}] (p', m'_A, m'_B) - \\ - RT \ln \gamma'_A [\underline{p}'_{r_A}, (\underline{m}'_A, \underline{m}'_B)_{r_A}] (p'_{r_A}, m'_A, m'_B) = \int_{p'_{r_A}}^{p'} v'_A (p', m'_A, m'_B) dp \quad (14)$$

and analogously for the other activity coefficients. Substitution of eqn. (14) in eqn. (12) gives:

$$RT \ln K_m = RT \ln K + RT \ln \frac{\{\gamma'_B [\underline{p}'_{r_B}, (\underline{m}'_A, \underline{m}'_B)_{r_B}] (p'_{r_B}, m'_A, m'_B)\}^{z_A}}{\{\gamma'_A [\underline{p}'_{r_A}, (\underline{m}'_A, \underline{m}'_B)_{r_A}] (p'_{r_A}, m'_A, m'_B)\}^{z_B}} - \\ - RT \ln \frac{\{\gamma''_B [\underline{p}''_{r_B}, (\underline{m}''_A, \underline{m}''_B)_{r_B}] (p''_{r_B}, m''_A, m''_B)\}^{z_A}}{\{\gamma''_A [\underline{p}''_{r_A}, (\underline{m}''_A, \underline{m}''_B)_{r_A}] (p''_{r_A}, m''_A, m''_B)\}^{z_B}} + \\ + z_A \int_{p'_{r_B}}^{p'} v'_B (p', m'_A, m'_B) dp - z_B \int_{p'_{r_A}}^{p'} v'_A (p', m'_A, m'_B) dp - \\ - z_A \int_{p''_{r_B}}^{p''} v''_B (p'', m''_A, m''_B) dp + z_B \int_{p''_{r_A}}^{p''} v''_A (p'', m''_A, m''_B) dp. \quad (15)$$

In the ion exchange equilibrium, the ion exchanger phase is denoted by '' and the solution phase by '. The only pressure operating on the solution is the atmospheric pressure, which is taken to be constant, i.e. $p' = 1$. On the ion exchanger phase, on the other hand, we have a pressure p'' equal to the sum of the swelling pressure (= the difference between the osmotic pressures of the ion exchanger phase and the surrounding solution) and the atmospheric pressure. Then, choosing $p'_{r_A} = p''_{r_A} = p'_{r_B} = p''_{r_B} = 1 = p'$, eqn. (12) may be written:

$$\ln K_m = \ln K + \ln \frac{\{\gamma'_B [1, (\underline{m}'_A, \underline{m}'_B)_{r_B}] (1, m'_A, m'_B)\}^{z_A}}{\{\gamma'_A [1, (\underline{m}'_A, \underline{m}'_B)_{r_A}] (1, m'_A, m'_B)\}^{z_B}} - \ln \frac{\{\gamma''_B [1, (\underline{m}''_A, \underline{m}''_B)_{r_B}] (p'', m''_A, m''_B)\}^{z_A}}{\{\gamma''_A [1, (\underline{m}''_A, \underline{m}''_B)_{r_A}] (p'', m''_A, m''_B)\}^{z_B}}. \quad (12a)$$

In eqn. (15) the first two integrals become zero:

$$RT \ln K_m = RT \ln K + RT \ln \frac{\{\gamma'_B [1, (\underline{m}'_A, \underline{m}'_B)_{r_B}] (1, m'_A, m'_B)\}^{z_A}}{\{\gamma'_A [1, (\underline{m}'_A, \underline{m}'_B)_{r_A}] (1, m'_A, m'_B)\}^{z_B}} - RT \ln \frac{\{\gamma''_B [1, (\underline{m}''_A, \underline{m}''_B)_{r_B}] (1, m''_A, m''_B)\}^{z_A}}{\{\gamma''_A [1, (\underline{m}''_A, \underline{m}''_B)_{r_A}] (1, m''_A, m''_B)\}^{z_B}} + \int_1^{p''} \{z_B v''_A (p'', m''_A, m''_B) - z_A v''_B (p'', m''_A, m''_B)\} dp. \quad (15a)$$

a) For the special case of the same reference state for each ion (e.g. infinitely dilute solution in the phase ') in both phases, then $p_{r_A} = p''_{r_A} = p_{r_A}$ and $(\underline{m}'_A, \underline{m}'_B)_{r_A} = (\underline{m}''_A, \underline{m}''_B)_{r_A} = (\underline{m}_A, \underline{m}_B)_{r_A}$ and $\mu_A^0 = \mu_A'^0$ and analogously for B, both terms on the right of eqn. (9) are zero or:

$$\frac{\{a'_A [p_{r_A}, (\underline{m}_A, \underline{m}_B)_{r_A}] (p', m'_A, m'_B)\}^{z_B}}{\{a''_A [p_{r_A}, (\underline{m}_A, \underline{m}_B)_{r_A}] (p'', m''_A, m''_B)\}^{z_B}} \cdot \frac{\{a''_B [p_{r_B}, (\underline{m}_A, \underline{m}_B)_{r_B}] (p'', m''_A, m''_B)\}^{z_A}}{\{a'_B [p_{r_B}, (\underline{m}_A, \underline{m}_B)_{r_B}] (p', m'_A, m'_B)\}^{z_A}} = 1 \quad (16)$$

which is of the same form as eqn. (10) but with $K=1$. (Note that not all the activities in eqn. (16) are identical with the corresponding ones in eqn. (10).) Eqn. (16), being the most common formulation of the Gibbs-Donnan equilibrium, reduces to the approximate expression first formulated by Donnan [1], if all activity coefficients are put equal to unity. Combination of eqns. (16) and (11) gives:

$$\ln K_m = \ln \frac{\{\gamma'_B [p_{r_B}, (\underline{m}_A, \underline{m}_B)_{r_B}] (p', m'_A, m'_B)\}^{z_A}}{\{\gamma'_A [p_{r_A}, (\underline{m}_A, \underline{m}_B)_{r_A}] (p', m'_A, m'_B)\}^{z_B}} - \ln \frac{\{\gamma''_B [p_{r_B}, (\underline{m}_A, \underline{m}_B)_{r_B}] (p'', m''_A, m''_B)\}^{z_A}}{\{\gamma''_A [p_{r_A}, (\underline{m}_A, \underline{m}_B)_{r_A}] (p'', m''_A, m''_B)\}^{z_B}}. \quad (17)$$

Introduction of pressure-independent activity coefficients results in an equation quite analogous to (15):

$$\begin{aligned}
RT \ln K_m = RT \ln & \frac{\{\gamma'_B [p_{r_B}, (\underline{m}_A, \underline{m}_B)_{r_B}] (p_{r_B}, m'_A, m'_B)\}^{z_A}}{\{\gamma'_A [p_{r_A}, (\underline{m}_A, \underline{m}_B)_{r_A}] (p_{r_A}, m'_A, m'_B)\}^{z_B}} - \\
& - RT \ln \frac{\{\gamma''_B [p_{r_B}, (\underline{m}_A, \underline{m}_B)_{r_B}] (p_{r_B}, m''_A, m''_B)\}^{z_A}}{\{\gamma''_A [p_{r_A}, (\underline{m}_A, \underline{m}_B)_{r_A}] (p_{r_A}, m''_A, m''_B)\}^{z_B}} + \\
& + z_A \int_{p_{r_B}}^{p'} v'_B(p', m'_A, m'_B) dp - z_B \int_{p_{r_A}}^{p'} v'_A(p', m'_A, m'_B) dp - \\
& - z_A \int_{p_{r_B}}^{p''} v''_B(p'', m''_A, m''_B) dp + z_B \int_{p_{r_A}}^{p''} v''_A(p'', m''_A, m''_B) dp. \quad (18)
\end{aligned}$$

When dealing with ion exchange equilibria we choose $p_{r_A} = p_{r_B} = 1 = p'$. Then, eqn. (17) may be written:

$$\begin{aligned}
\ln K_m = \ln & \frac{\{\gamma'_B [1, (\underline{m}_A, \underline{m}_B)_{r_B}] (1, m'_A, m'_B)\}^{z_A}}{\{\gamma'_A [1, (\underline{m}_A, \underline{m}_B)_{r_A}] (1, m'_A, m'_B)\}^{z_B}} - \\
& - \ln \frac{\{\gamma''_B [1, (\underline{m}_A, \underline{m}_B)_{r_B}] (p'', m''_A, m''_B)\}^{z_A}}{\{\gamma''_A [1, (\underline{m}_A, \underline{m}_B)_{r_A}] (p'', m''_A, m''_B)\}^{z_B}}. \quad (17a)
\end{aligned}$$

In eqn. (18) the first two integrals become zero:

$$\begin{aligned}
RT \ln K_m = RT \ln & \frac{\{\gamma'_B [1, (\underline{m}_A, \underline{m}_B)_{r_B}] (1, m'_A, m'_B)\}^{z_A}}{\{\gamma'_A [1, (\underline{m}_A, \underline{m}_B)_{r_A}] (1, m'_A, m'_B)\}^{z_B}} - \\
& - RT \ln \frac{\{\gamma''_B [1, (\underline{m}_A, \underline{m}_B)_{r_B}] (1, m''_A, m''_B)\}^{z_A}}{\{\gamma''_A [1, (\underline{m}_A, \underline{m}_B)_{r_A}] (1, m''_A, m''_B)\}^{z_B}} + \\
& + \int_1^{p''} \{z_B v''_A(p'', m''_A, m''_B) - z_A v''_B(p'', m''_A, m''_B)\} dp. \quad (18a)
\end{aligned}$$

2. The reference states are functions of the pressure in the corresponding phase. When defining an activity coefficient of an electrolyte solution, a constant composition at the same (temperature and) pressure as that of the solution considered is often chosen as the reference state. A change in external pressure on the solution will consequently result in a change of the reference state. In this connection, it is only of interest to regard the case where the compositions of the reference states in both phases are equal, i.e. $(\underline{m}'_A, \underline{m}'_B)_{r_A} = (\underline{m}''_A, \underline{m}''_B)_{r_A} = (\underline{m}_A, \underline{m}_B)_{r_A}$ and analogously for B. Thus, we have for example:

$$\mu_A^0 [p'_{r_A}, (\underline{m}'_A, \underline{m}'_B)_{r_A}] = \mu_A^0 [p', (\underline{m}_A, \underline{m}_B)_{r_A}] = f_A(p').$$

This choice of reference states agrees in principle with that made by Donnan and Guggenheim in their detailed thermodynamical treatment of the Gibbs-Donnan equilibrium [8, 9].

Integration of:

$$\frac{\partial \mu_A^0 [p, (\underline{m}_A, \underline{m}_B)_{r_A}]}{\partial p} = v_A^0 [p, (\underline{m}_A, \underline{m}_B)_{r_A}] \quad (19)$$

gives a relation between μ_A^0 and $\mu_A'^0$:

$$\mu_A'^0 [p'', (\underline{m}_A, \underline{m}_B)_{r_A}] - \mu_A^0 [p', (\underline{m}_A, \underline{m}_B)_{r_A}] = \int_{p'}^{p''} v_A^0 [p, (\underline{m}_A, \underline{m}_B)_{r_A}] dp \quad (20)$$

which together with the corresponding relation for B and substitution in eqn. (9) gives:

$$RT \ln \left\{ \left(\frac{a'_A [p', (\underline{m}_A, \underline{m}_B)_{r_A}]}{a''_A [p'', (\underline{m}_A, \underline{m}_B)_{r_A}]} \right)^{z_B} \cdot \left(\frac{a''_B [p'', (\underline{m}_A, \underline{m}_B)_{r_B}]}{a'_B [p', (\underline{m}_A, \underline{m}_B)_{r_B}]} \right)^{z_A} \right\} \\ = \int_{p'}^{p''} \{ z_B v_A^0 [p, (\underline{m}_A, \underline{m}_B)_{r_A}] - z_A v_B^0 [p, (\underline{m}_A, \underline{m}_B)_{r_B}] \} dp \quad (21)$$

The activities in this equation are not identical with the corresponding activities in either eqn. (10) or eqn. (16) as is obvious from the notation and also from the fact that the right hand side of eqn. (21) is not a constant. Combining eqns. (21) and (11) we have:

$$RT \ln K_m = RT \ln \frac{\{\gamma'_B [p', (\underline{m}_A, \underline{m}_B)_{r_B}] (p', m'_A, m'_B)\}^{z_A}}{\{\gamma'_A [p', (\underline{m}_A, \underline{m}_B)_{r_A}] (p', m'_A, m'_B)\}^{z_B}} - \\ - RT \ln \frac{\{\gamma''_B [p'', (\underline{m}_A, \underline{m}_B)_{r_B}] (p'', m''_A, m''_B)\}^{z_A}}{\{\gamma''_A [p'', (\underline{m}_A, \underline{m}_B)_{r_A}] (p'', m''_A, m''_B)\}^{z_B}} + \\ + \int_{p'}^{p''} \{ z_B v_A^0 [p, (\underline{m}_A, \underline{m}_B)_{r_A}] - z_A v_B^0 [p, (\underline{m}_A, \underline{m}_B)_{r_B}] \} dp \quad (22)$$

In eqn. (22) as in eqns. (12) and (17) the activity coefficients depend on the pressure in the corresponding phase. Introduction of pressure-independent activity coefficients by means of eqn. (7) gives eqn. (18). Taking $p' = \text{const.} = 1$ as in the cases treated before, eqn. (22) may be written:

$$RT \ln K_m = RT \ln \frac{\{\gamma'_B [1, (\underline{m}_A, \underline{m}_B)_{r_B}] (1, m'_A, m'_B)\}^{z_A}}{\{\gamma'_A [1, (\underline{m}_A, \underline{m}_B)_{r_A}] (1, m'_A, m'_B)\}^{z_B}} - \\ - RT \ln \frac{\{\gamma''_B [p'', (\underline{m}_A, \underline{m}_B)_{r_B}] (p'', m''_A, m''_B)\}^{z_A}}{\{\gamma''_A [p'', (\underline{m}_A, \underline{m}_B)_{r_A}] (p'', m''_A, m''_B)\}^{z_B}} + \\ + \int_1^{p''} \{ z_B v_A^0 [p, (\underline{m}_A, \underline{m}_B)_{r_A}] - z_A v_B^0 [p, (\underline{m}_A, \underline{m}_B)_{r_B}] \} dp \quad (22a)$$

From the thermodynamical point of view, eqns. (10), (12), (15), (16), (17), (18), (21), and (22) are of course completely equivalent as they are all deduced from the general equilibrium equation (9). The formal differences are *only* due to the different choices of reference states. As pointed out above, this has not been completely realized by some authors. A common mistake is to regard eqn. (16) as an approximation [10, 11]. This is not true, of course, provided that the activity coefficients are correctly defined. On the other hand these different reference states will result in activity coefficients which are not directly comparable.

The activity coefficients entering the equilibrium expressions written above are single ion activity coefficients. Thus they are not determinable separately but only in those ratios which they enter the formulas. For an electrolyte dissociating into ν_+ cations and ν_- anions, the following equation holds generally for the experimentally accessible mean activity coefficient, $\gamma_{\pm}$

$$\gamma_{\pm}^{\nu} = \gamma_{+}^{\nu_{+}} \cdot \gamma_{-}^{\nu_{-}} \quad (23)$$

where $\nu = \nu_{+} + \nu_{-}$. Since $z_{+}\nu_{+} = z_{-}\nu_{-}$ where z_{+} and z_{-} are the valences of cation and anion, we have for two electrolytes with a common anion:

$$\frac{\gamma_B^{z_A}}{\gamma_A^{z_B}} = \frac{\gamma_{BX}^{z_A}}{\gamma_{AX}^{z_B}} \cdot \left(\frac{\gamma_{BX}}{\gamma_{AX}} \right)^{\frac{z_A z_B}{z_X}} \quad (24)$$

which for two 1-1 electrolytes reduces to:

$$\frac{\gamma_B}{\gamma_A} = \left(\frac{\gamma_{BX}}{\gamma_{AX}} \right)^2. \quad (24 a)$$

The single partial ionic molal volumes are likewise separately inaccessible. However, the following relation holds generally between the partial molal volumes of the electrolyte and its ions:

$$v_{AX} = \nu_A v_A + \nu_X v_X. \quad (25)$$

From this we obtain for two electrolytes with a common anion:

$$z_B v_A - z_A v_B = \frac{z_B v_{AX}}{\nu_A} - \frac{z_A v_{BX}}{\nu_B} \quad (26)$$

which for two 1-1 electrolytes reduces to:

$$v_A - v_B = v_{AX} - v_{BX}. \quad (26 a)$$

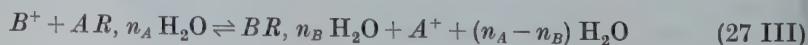
It may be mentioned that by applying eqn. (4) to the neutral electrolytes instead of eqn. (3) to the single ions, as has been done above, it is possible to derive equilibrium equations analogous to eqn. (9) and subsequent equations but containing the mean activity coefficients and partial volumes of the electrolytes instead of the corresponding single ion properties.

The ion exchange equilibrium regarded as a bimolecular, reversible reaction equilibrium

As has already been pointed out, an expression such as eqn. (10) is obtained when treating an ion exchange equilibrium as the equilibrium state of a bimolecular, reversible reaction. In this case, however, it is customary to consider the components AR_{z_A} and BR_{z_B} (where R refers to the univalent functional group of the ion exchanger) rather than the single ions A and B . As a consequence, the equilibrium equation will not contain any single ion activity coefficients for the ion exchanger phase but instead, the thermodynamically defined activity coefficients of the components AR_{z_A} and BR_{z_B} . This way of approach combined with the use of the Gibbs-Duhem equation on the ion exchanger phase was introduced by Ekedahl, Högfeldt and Sillén [12] and by Argersinger, Davidson and Bonner [13], independently. It is of interest to discuss some details of their treatment. In the first papers, the water activity and its variation were not taken into consideration. This problem has later been treated by Högfeldt [14], Gaines and Thomas [15], and Davidson and Argersinger [16], independently. For a comparison of the formulas for the activity coefficients in the ion exchanger and the thermodynamical equilibrium constants derived by these authors, the different choices of components in the ion exchanger phase and their reference states will be given in a manner which removes the slight ambiguities in the original papers. For simplicity, the comparison is confined to the equilibrium between two univalent ions, A and B .

- (I) Högfeldt [14]: Components in the ion exchanger are AR , BR and water. The activity coefficient of AR , $f_{AR}^I = 1$ in an ion exchanger saturated only with A and in equilibrium with an AX -solution of that molality at which the ion exchange equilibrium is studied; analogously for f_{BR}^I . The standard state of water (pure water) is the same in the ion exchanger and the surrounding solution, i.e. $a_w'' = a_w'$ at equilibrium.
- (II) Gaines *et al.* [15]: Components in the ion exchanger are AR , BR and water. $f_{AR}^{II} = 1$ in an A -saturated ion exchanger in equilibrium with an infinitely dilute AX -solution i.e. pure water; analogously for f_{BR}^{II} . The standard state of water is pure water in the ion exchanger and the surrounding solution.
- (III) Davidson *et al.* [16]: Components in the ion exchanger are AR , $n_A \text{H}_2\text{O}$ and BR , $n_B \text{H}_2\text{O}$ where n_A and n_B are the numbers of moles of water per equivalent ion exchanger completely saturated with A and B respectively. $f_{AR, n_A \text{H}_2\text{O}}^{III} = 1$ in an A -saturated ion exchanger in equilibrium with an AX -solution of that molality at which the ion exchange equilibrium is studied; analogously for $f_{BR, n_B \text{H}_2\text{O}}^{III}$. The standard state of water is pure water in the solution.

The ion exchange equilibrium is formulated according to the various authors, thus



from which the thermodynamical equilibrium constant:

$$K^I = \kappa \frac{f_{BR}^I}{f_{AR}^I} \quad (28 \text{ I})$$

and analogously for II, whilst

$$K^{III} = \kappa \frac{f_{BR, n_B \text{ H}_2\text{O}}^{III}}{f_{AR, n_A \text{ H}_2\text{O}}^{III}} \quad (28 \text{ III})$$

where $\kappa = N_B m_{A^+} \gamma_{AX}^2 / N_A m_{B^+} \gamma_{BX}^2$. N_A and N_B are the equivalent fractions of A and B , respectively, in the ion exchanger, m_{A^+} and m_{B^+} the molalities¹ of the same ions in the surrounding solution, and γ_{AX} and γ_{BX} the mean molal activity coefficients in the solution of the electrolytes AX and BX respectively. As N_A and N_B mean equivalent fractions and only the equilibrium between univalent ions is considered, N and thus κ will be independent of the choice of components and consequently identical in the treatments of the three groups of authors. The Gibbs-Duhem equation, $\sum_i n_i d\mu_i = 0$, applied to one equivalent of the ion exchanger gives after integration:

$$\ln f_{AR}^I(N_B) = N_B \ln \kappa(N_B) - \int_0^{N_B} \ln \kappa dN_B - \int_{a_w(N_B=0)}^{a_w(N_B)} n_w d \ln a_w \quad (29 \text{ I})$$

$$\begin{aligned} \ln f_{AR}^{II}(N_B) = N_B \ln \kappa(N_B) - \int_0^{N_B} \ln \kappa dN_B - \\ - \int_{a_w(N_B=0)}^{a_w(N_B)} n_w d \ln a_w + \int_{a_w=1(N_B=0)}^{a_w(N_B=0)} (V_A/\tau - n_w) d \ln a_w \end{aligned} \quad (29 \text{ II})$$

$$\ln f_{AR, n_A \text{ H}_2\text{O}}^{III}(N_B) = N_B \ln \kappa(N_B) - \int_0^{N_B} \ln \kappa dN_B + (n_A - n_B) \int_{a_w(N_B=0)}^{a_w(N_B)} N_B d \ln a_w \quad (29 \text{ III})$$

where a_w is the activity of water, n_w the number of moles of water per equivalent ion exchanger, V_A the volume of one equivalent A -saturated ion exchanger and τ the molar volume of water vapor. Analogous formulas are obtained for f_{BR} . The right hand side of eqns. (29 I) and (29 II) are identical except for the last term in eqn. (29 II)—this term is the value of $\ln f_{AR}^{II}$ in an ion exchanger completely saturated with A ions and in equilibrium with an AX -solution of the molality at which the equilibrium is studied. This term was obtained from the general equilibrium equation

$$V dp = \sum_i n_i d\mu_i \quad (\text{at constant temperature})$$

which in this case can be written:

¹ We disregard the fact that Högfelt really expresses the solution concentrations in molalities instead of molalities as this is unimportant for the present discussion.

$$V_A dp = d \ln f_{AR}^{\text{II}} + n_w d \ln a_w \quad (\text{for the pure } A\text{-saturated ion exchanger})$$

and

$$\tau dp = d \ln a_w \quad (\text{for the vapor phase}).$$

Elimination of dp and subsequent integration gives the required value of $\ln f_{AR}^{\text{II}}$ [15].

For cation exchangers of the polystyrene sulfonic acid type (PSS ion exchangers) with a divinylbenzene (DVB) content of over 6% at least, V_A/τ is less than one per cent of n_w [17, 18]; i.e. it is of about the same magnitude as the experimental error in n_w , and may consequently be neglected. Thus, we obtain:

$$\ln f_{AR}^{\text{I}}(N_B) \cong \ln f_{AR}^{\text{II}}(N_B) + \int_{a_w=1(N_B=0)}^{a_w(N_B=0)} n_w d \ln a_w. \quad (30 \text{ I, II})$$

From the choices of reference states it is obvious that the values of f_{AR}^{I} obtained at different concentrations of the external solution are not comparable. By means of eqn. (30 I, II) it is, however, possible to convert f_{AR}^{I} into f_{AR}^{II} , the reference state of which is independent of concentration. A good estimate of the last term in eqn. (30 I, II) may be made by considering $n_w \cong n_A$ (= constant), when a_w changes from 1 ($N_B=0$; surrounding solution = pure water) to a_w ($N_B=0$; surrounding solution = AX -solution of the molality at which the equilibrium is studied).

The activity coefficient $f_{AR, n_A \text{ H}_2\text{O}}^{\text{III}}$ is a priori less general than f_{AR}^{I} and f_{AR}^{II} since Davidson's *et al.* choice of components rests on the assumption that the water sorption in a PSS ion exchanger with a certain DVB content saturated with two univalent ions is a linear function of the equivalent fraction of one of the two ions. This relation $n_w = n_A + (n_B - n_A) N_B$ has been experimentally proved only for $\text{NH}_4^+ - \text{H}^+$ [19] and $\text{Na}^+ - \text{Cs}^+$ [20], but not for any case where one of the ions has not the rare gas electronic structure. In the latter case, a deviation from linearity may occur. Introducing, however, the approximate relation $n_w = n_A + (n_B - n_A) N_B$ in eqn. (29 III) and combining with eqn. (29 I) we have:

$$\ln f_{AR}^{\text{I}}(N_B) = \ln f_{AR, n_A \text{ H}_2\text{O}}^{\text{III}}(N_B) - n_A \int_{a_w(N_B=0)}^{a_w(N_B)} d \ln a_w. \quad (30 \text{ I, III})$$

If a_w is independent of N_B , which is approximatively true for the pair $\text{Ag}^+ - \text{H}^+$ for example if the concentration of the external solution is less than 0.1 molar [14], eqn. (30 I, III) reduces to

$$f_{AR}^{\text{I}} \cong f_{AR, n_A \text{ H}_2\text{O}}^{\text{III}}.$$

Combination of eqns. (28) and (29) and the expressions for B corresponding to eqn. (29) gives:

$$\ln K^{\text{I}} = \int_0^1 \ln \kappa dN_B + \int_{a_w(N_B=0)}^{a_w(N_B=1)} n_w d \ln a_w \quad (31 \text{ I})$$

$$\ln K^{\text{II}} = \int_0^1 \ln \kappa dN_B + \int_{a_w(N_B=0)}^{a_w(N_B=1)} n_w d \ln a_w - \\ - \int_{a_w=1(N_B=1)}^{a_w(N_B=1)} n_w d \ln a_w + \int_{a_w=1(N_B=0)}^{a_w(N_B=0)} n_w d \ln a_w \quad (31 \text{ II})$$

(if $V_A/\tau \ll n_w \gg V_B/\tau$, cf. p. 19) and

$$\ln K^{\text{III}} = \int_0^1 \ln \kappa dN_B + (n_A - n_B) \ln a_w(N_B=1) - (n_A - n_B) \int_{a_w(N_B=0)}^{a_w(N_B=1)} N_B d \ln a_w. \quad (31 \text{ III})$$

Introducing the approximate relation $n_w = n_A + (n_A - n_B)N_B$ in eqn. (31 III) and combining with eqn. (31 II), we obtain:

$$\ln K^{\text{II}} = \ln K^{\text{III}} - \int_{a_w=1(N_B=1)}^{a_w(N_B=1)} n_w d \ln a_w + \int_{a_w=1(N_B=0)}^{a_w(N_B=0)} n_w d \ln a_w + \\ + n_B \ln a_w(N_B=1) - n_A \ln a_w(N_B=0). \quad (32 \text{ II, III})$$

With the approximation mentioned above: $n_w \cong n_A$ (= constant) in the interval $a_w=1(N_B=0)$ to $a_w(N_B=0)$ and analogously $n_w \cong n_B$ (= constant) in the interval $a_w=1(N_B=1)$ to $a_w(N_B=1)$, eqn. (32 II, III) reduces to

$$\ln K^{\text{II}} \cong \ln K^{\text{III}}.$$

Summing up we find that of the alternatives I, II and III the one due to Gaines and Thomas [15] (II) is the most advantageous since it results in activity coefficients in the ion exchanger phase which are independent of the concentration of the external solution. The pressure dependence of the activity coefficients is, however, common to all three alternatives. Furthermore both the pressure and the composition (for alternative III the components, i.e. n_A and n_B) of the reference states are changed by a change in the degree of crosslinking of the ion exchanger. It is thus of interest to know how great this disadvantage is, i.e. if the pressure dependence of the activity coefficients has any significance compared with the dependence on ionic interaction.

Summary

A general thermodynamical equilibrium equation is derived for the ion exchange equilibrium by treating it as a Gibbs-Donnan equilibrium, eqn. (9). (For explanation of symbols see List of symbols and Table 1.) From this general equation, the following special cases are discussed both for pressure-dependent and pressure-independent activity coefficients. In all these cases the compositions of the reference states are taken as constant.

1. The reference states are independent of pressure. For pressure-dependent activity coefficients, the equilibrium equation, eqns. (10) and (11), is identical

with the one most commonly derived from the law of mass action. If, in addition, the reference states are the same in both phases, this equation reduces to an equilibrium equation, eqns. (16) and (17), identical with the most common form of the Donnan equilibrium.

2. Each reference state is a function of the pressure in the corresponding phase, eqns. (21) and (22). The equation for this case with pressure-dependent activity coefficients, eqn. (22), has often been confused with the analogous equation with pressure-independent activity coefficients, eqn. (18).

For the special case of ion exchange resins, the relations between the different activity coefficients and the thermodynamical equilibrium constants derived from the law of mass action, for the different choices of reference states and components in the ion exchanger phase made by different authors, are discussed, eqns. (27) to (30).

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The reaction of tributyl arsenite with benzylmagnesium chloride

By SVEN-OLOV LAWESSON

In continuing a work on arsonic acids as plant growth regulators (1), the author has tried to prepare α (1- respectively 2-naphthyl)-ethylarsonic acids from the corresponding halides by applying the Meyer reaction (2). Only hydrocarbons were obtained, however, without a trace of the desired product. The Meyer reaction seems to be too rough with secondary aliphatic halides, and apparently tends to give side reactions such as dehydrohalogenation. In a comparison with the corresponding phosphorus compounds, it may be mentioned that a reaction of organic secondary halides with metal salts of phosphites yielded only olefins (3).

In 1929 (4), it was reported (although no experimental details were given) that the reaction of triethyl arsenite and phenylmagnesium bromide yielded 85.3 % of triphenylarsine. The same year, Challenger and Peters (4) reported that benzylmagnesium chloride and arsenic trichloride gave a good yield of tribenzylarsine, with smaller amounts of tribenzylarsine oxide and dibenzylarsinic acid. In view of the above results, it could be expected that the reaction of a Grignard reagent with trialkyl arsenite might provide a satisfactory route to arsonic acids if performed at low temperature, and according to the "reversed" Grignard reaction. Experiments were made with benzyl chloride, which is cheap and easy to obtain. Initially, equimolar amounts of tributyl arsenite and benzylmagnesium chloride were brought together in ether; from the mixture were isolated dibenzylarsinic acid (26 %), tribenzylarsine (7 %) and dibenzyl (11 %). If the reaction was carried out with a 2:1 molar ratio of the arsenite to the Grignard reagent, the same products were isolated. Yields: 33 %, 8 %, and 13 %, respectively. No benzylarsonic acid could be isolated.

A few years ago Dawson and Burger (6, 7) isolated phosphonic acids in good yields from the reaction of dialkylchloro phosphates with benzylmagnesium halides. Dialkylchloro phosphates were chosen as reagents for the Grignard synthesis because the ester groups could be expected to have lower affinity to Grignard reagents and the lone chlorine atom to be eliminated first, with establishment of a carbon-to-phosphorus linkage.

Only a few esters of pentavalent arsenic are known, but as with arsenious acid, no ester-acids, such as $\text{AsO}(\text{OCH}_3)_2\text{OH}$. Nor are any dialkylhalo arsenates known. By the action of chlorine on tributyl arsenite, a colourless oil was obtained, which decomposed on standing, or on attempted distillation; of its identity there can be some doubt, however, since it did not react with amines to give the corresponding aminoarsonates.

We have tried to apply the Michaelis-Arbuzov reaction to trivalent arsenic but without success.

The work on arsonic acids as plants growth regulators will not be continued by the author.

Experimental

Tributyl arsenite

Azeotropic esterification of butyl alcohol and excess of arsenic trioxid, using benzene as the water-entrainer, was carried to the point where all the water azeotrope had been removed, giving a colourless oil. Yield 74 %. B.p. 98–100°C/1 mm. Some decomposition occurred during the distillation.

α -(2-Naphthyl)-ethylchloride

In 35 ml of dry ether was dissolved 17.5 g of methyl-(2-naphthyl)-carbinol (8) and the solution poured slowly, with thorough cooling, into 20 g of thionylchloride in 75 ml of dry ether. The solution was allowed to stand at room temperature for two hours, whereupon the ether and the excess of thionylchloride were removed under reduced pressure. The residue was treated with ice and water and then extracted with ether. The extract was washed with dilute sodium bicarbonate, then with water and finally dried over sodium sulphate. The ether was removed, the residue distilled and the fraction, b.p. 124°C/2 mm collected. Yield 82 %. A crystallization from ligroin (b.p. 40–60°C) gave white plates, m.p. 59–61°C.

Anal. Subst. 62.60 mg; 4.43 ml of 0.0739*M* NaOH.

27.40 mg; 75.68 mg of CO₂; 13.95 mg of H₂O.

C₁₂H₁₁Cl (190.67) Calc. C 75.59 %; H 5.82 %; Cl 18.60 %.

Found C 75.41 %; H 5.69 %; Cl 18.50 %.

The new compound, not previously reported in literature, seems to be unstable. After a couple of months it began to sweat, became discoloured and the melting point became lower.

The Meyer reaction

Equimolar amounts of α (naphthyl)-ethylchloride and 10*M* sodium arsenite were refluxed with stirring for 5 hours. The water layer was separated and carefully acidified with hydrochloric acid; no arsonic acid had been formed. The same amounts of the reactants were shaken at room temperature for 6 days. No reaction took place and the reactants were recovered.

The Grignard reaction

Benzylmagnesium chloride, prepared from 25.8 g of benzyl chloride and 5 g of magnesium, in 120 ml of ether, was added dropwise with stirring during 2 hours to 80 g of tributyl arsenite in 150 ml of ether at –70°C. The mixture was gradually treated with crushed ice and sulfuric acid. A solid, not soluble in ether or water + acid, was obtained. The aqueous layer was washed once with ether, the organic layers

were combined, washed with water and dried over sodium sulfate. A solid was collected from the dried ether, after evaporation to half the volume, and recrystallization from ethanol gave 4.8 g of tributylarsine, m.p. 102–104°C.

Anal. Subst. 53.40 mg; 11.61 ml of 0.004447M KBrO₃.

21.30 mg; 56.60 mg of CO₂; 11.33 mg of H₂O.

C₂₁H₂₁As (348.28) Calc. C 72.41 %; H 6.08 %; As 21.51 %.

Found C 72.50 %; H 5.97 %; As 21.62 %.

The ether solution was evaporated to a pale green-yellow oil (27 g). This was distilled to give 17 g of butanol (b.p. 117–124°C/760 mm) and the rest, after crystallization from ethanol, gave dibenzyl (4.1 g) m.p. and mixed m.p., 52–54°C.

The water-insoluble solid was recrystallized from ethanol as white plates. Some arsenic trioxide (4 g) was isolated and the rest was 12.9 g of dibenzylarsinic acid. M.p. 208–210°C.

Anal. Subst. 64.30 mg; 16.60 ml of 0.004447M KBrO₃.

24.60 mg; 52.62 mg of CO₂; 11.74 mg of H₂O.

C₁₄H₁₅O₂As (290.17) Calc. C 57.94 %; H 5.21 %; As 25.82 %.

Found C 58.11 %; H 5.29 %; As 25.70 %.

The aqueous layers were combined and extracted with ether; evaporation of the dried extract gave an oil which partly crystallized. Dibenzylarsinic acid (0.9 g) separated from ethanol as plates.

The aqueous layer was made alkaline with sodium carbonate and the precipitated magnesium carbonate filtered off. The filtrate was concentrated to half its initial volume and acidified with sulfuric acid; it was then extracted with ether, and evaporation of the dried extract gave 1.6 g of dibenzylarsinic acid. The aqueous layer was finally evaporated to dryness. The solid residue was exhaustively extracted, successively with ether and dry ethanol, but evaporation of the extracts gave in each case only a trace of gum.

Attempts to prepare dibutylchloro arsenate

Tributyl arsenite (77 g), dissolved in dry carbon tetrachloride (200 ml) was cooled to –15°C, and chlorine was slowly passed through until a yellow colouration persisted. This took place when the gain in weight was equal to 18 g. After 5 minutes thoroughly dried air was drawn through until the liquid was colourless. Dry, powdered, lead carbonate was then added in small quantities and air drawn through the mixture for 12 hours or more. Unfortunately, the complete removal of the hydrogen chloride was never manifested; the mixture was always strongly acidic. Adherent hydrogen chloride made analysis of the ester unsatisfactory, and on distillation, decomposition was likely. However, a fraction (53 g) was collected, b.p. 129–131°C/1 mm, to which no simple structure could be assigned.

The Michaelis-Arbuzov reaction

Equimolar amounts of tributyl arsenite and benzyl chloride were mixed, and refluxed for several hours. The reactants were recovered. Nor did any desired reaction take place when we used a secondary halide.

Summary

Dibenzylarsinic acid and tribenzylarsine were obtained from benzylmagnesium chloride and tributyl arsenite under varying conditions. Benzylarsonic acid cannot be prepared in this way.

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Diethanolamine esters of alkylboronic acids

BY SVEN-OLOV LAWESSON

With 2 figures in the text

The synthesis of certain alkylboronic acids by controlled oxidation of trialkylborines was first described by Frankland (1); later, by Krause and coworkers (2, 3), and by Johnson and Van Campen (4):

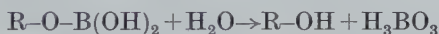
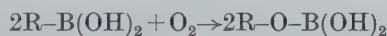


Khotinsky and Melamed (5) prepared boronic acids according to the reaction:



Krause (6) employed boron trifluoride instead of an alkyl borate.

The aliphatic boronic acids lose water with great ease and resemble aliphatic aldehydes in many ways; e.g. they combine with molecular oxygen:



Water, however, inhibits the autooxidation.

One year ago, the author made an attempt to prepare 1- and 2-naphtylmethylboronic acids in order to investigate them as plant growth regulators. However, it was found that the acids were very unstable in the dry state, although they remained unchanged in presence of water (in cold). The result was not unexpected, for earlier (7, 8), benzylboronic acid had been reported to be oxidized very easily by air, and oxygen must be excluded during its manipulation. Secondary and tertiary boronic acids also have the same properties. Primary aliphatic boronic acids, reported in the literature by different authors, have not consistent melting points. This indicates to some extent oxidation of the acids giving a mixture of boric and boronic acids.

Recently, Torssell (9) reported the alkylesters of arylboronic acids to be easily hydrolyzable by moist air, and Letsinger and Skoog (10) the diethanolamine esters of a few aromatic acids to be solid. Musgrave and Park (11) reported, when this investigation was completed, a study in diethanolamine esters of some phenylboronic acids. We have investigated the diethanolamine esters of aliphatic boronic acids (Table I) and have found them to be stable in air for months in the dry state, to have

Table 1. Diethanolamine esters of alkylboronic acids.

Boronic acid R-B(OH) ₂	Derivatives		Carbon**		Hydrogen		Boron	
	Yield (%)	M.p. (°C)	Calcd.	Found	Calcd.	Found	Calcd.	Found
R = ethyl	77	161-163	50.39	49.9	9.87	9.71	7.57	7.61
n-propyl	74	155-157	53.54	53.0	10.3	10.0	6.89	6.84
i-propyl*	58	196-198	53.54	53.1	10.3	10.5	6.89	6.86
n-butyl	70	153-155	56.17	55.8	10.6	10.9	6.33	6.29
i-butyl	59	152-154	56.17	55.9	10.6	10.6	6.33	6.36
t-butyl	52	220-222	56.17	55.9	10.6	10.6	6.33	6.37
n-amyl	68	152-154	58.40	58.0	10.9	10.9	5.85	5.90
i-amyl	60	141-143	58.40	58.1	10.9	10.8	5.85	5.90
n-hexyl	67	125-127	60.32	59.7	11.1	11.5	5.43	5.45
benzyl	55	211-213	64.43	64.1	7.86	7.71	5.28	5.24
1-naphthylmethyl*	90	196-198	70.68	70.2	7.11	7.32	4.24	4.28
2-naphthylmethyl*	90	229-231	70.68	70.0	7.11	7.17	4.24	4.25

* Earlier not reported.

** The carbon analyses were complicated by the formation of boron carbides.

reproducible and sharp melting points, and to form well defined crystals. They are insoluble in ether, ligroin, carbon tetrachloride, and carbon disulfide, and slightly soluble in water and acetone.

The boronic acids were prepared by treating tributyl borate in ether, with an equimolar amount of the Grignard reagent in ether solution, at -60° . After acid hydrolysis, the organic layer was shaken with sodium hydroxide solution, the aqueous extract acidified with hydrochloric acid and the precipitated acid esterified with diethanolamine, using benzene as water-entrainer. In one experiment, the boronic acid was prepared from the lithium reagent. The yield, however, was not increased appreciably.

The stability of the esters mentioned above is extraordinary, in comparison with that of the acids. We had, therefore, to suspect, as a possible explanation, either hydrogen bonding or some coordination between the boron and nitrogen atoms. Co-

ordination of $\begin{array}{c} \diagup \\ \text{---N:} \\ \diagdown \end{array}$ with $\begin{array}{c} \text{O} \\ \diagup \\ \text{B---O} \\ \diagdown \\ \text{O} \end{array}$ across an eight-membered ring in triethanolamine

borate has earlier been demonstrated (12). Recently (13), an examination of the N-H frequencies of salts of $[(\text{C}_2\text{H}_5)_x \cdot \text{NH}_y]^+ (\text{C}_6\text{H}_5)_4\text{B}^-$ type (where $x+y=4$) was reported (no details are given) and it was found that, for non-hydrogen-bonded N-H, frequencies are near 3100 cm^{-1} . It is to be noted, in this case, that the nitrogen is quadri-covalent.

In order to get a measure of the N-H shift of a true coordination compound, diethylamine-, dipropylamine- and piperidine-boron trifluorides were prepared by modifying the method of Kraus and Brown (14). A comparison of the infrared spectra of the amines and the corresponding coordination compounds showed a lowering of the N-H frequencies of $0-50\text{ cm}^{-1}$. For $\text{NH}_3:\text{BF}_3$ $\Delta\nu=62\text{ cm}^{-1}$ (14).

Using pressed potassium bromide, the infrared spectra of the diethanolamine esters were obtained (Table 2).

Table 2. The bonded N-H frequencies of diethanolamine esters of alkylboronic acids.

Ester $R-B(OCH_2 \cdot CH_3)_3NH$	ν (cm ⁻¹) N-H
R = ethyl	3,120
<i>n</i> -propyl	3,080
<i>i</i> -propyl	3,080
<i>n</i> -butyl	3,080
<i>i</i> -butyl	3,080
<i>t</i> -butyl	3,100
<i>n</i> -amyl	3,070
<i>i</i> -amyl	3,070
<i>n</i> -hexyl	3,060
benzyl	3,050
1-naphthylmethyl	3,090
2-naphthylmethyl	3,090

(Non-bonded N-H frequencies $\approx 3,300$ cm⁻¹.)

The lowering of the fundamental stretching frequencies, generally a shift of 250–180 cm⁻¹, is very strong, but when compared with the 0–50 cm⁻¹ shift mentioned above between secondary amines and their corresponding boron trifluoride coordination compounds, it cannot be accounted for by the occurrence of transannular interaction across the eight-membered ring. Instead, we have hydrogen-bonding. In order to differentiate between inter- and intramolecular hydrogen-bonding, we determined a series of spectra at different dilutions. Fig. 2 shows the spectra of such a series for the diethanolamine ester of *n*-propylboronic acid dissolved in chloroform. As the concentration decreases (from the bottom to the top), the bonded absorption near 3100

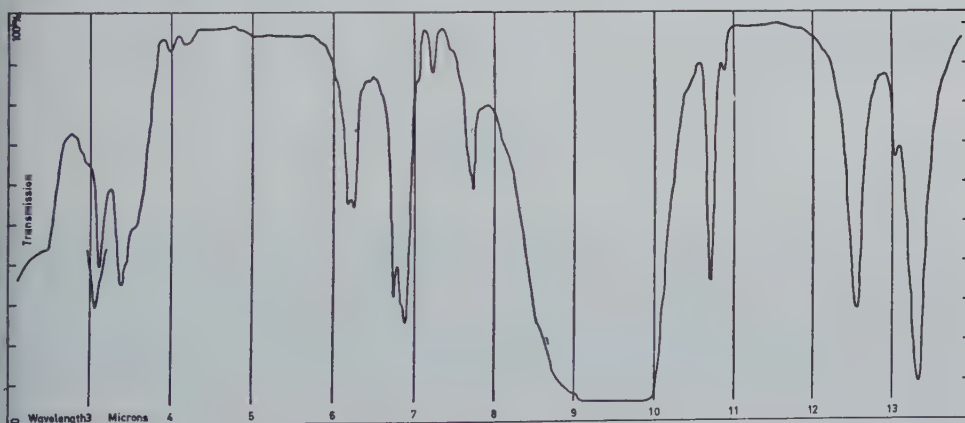


Fig. 1. The infrared spectrum of $\begin{matrix} C_3H_7 & H \\ & \diagdown \quad \diagup \\ & N : BF_3 \\ & \diagup \quad \diagdown \\ C_3H_7 & \end{matrix}$ (in pressed KBr) and the N-H band of $\begin{matrix} C_3H_7 \\ & \diagdown \\ & NH (liq). \\ C_3H_7 \end{matrix}$

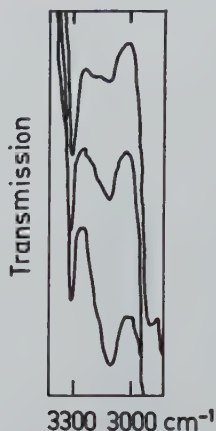


Fig. 2. The effect of intermolecular hydrogen bonding on infrared absorption.

Intermolecular H-bonding

cm^{-1} disappears while the unbonded absorption near 3330 cm^{-1} increases. This strongly suggests intermolecular hydrogen-bonding. Furthermore, an existing bond between the nitrogen and boron atoms ought to be indicated by a new band near 3250 cm^{-1} . The curves in Fig. 2 do not show any such indications, however.

According to these results, it must be concluded that intermolecular hydrogen-bonding in diethanolamine esters of aliphatic boronic acids is predominant, and that

a coordination $\begin{array}{c} \delta^+ \quad \delta^- \\ \diagdown \quad \diagup \\ \text{—N:} \curvearrowright \text{B—} \\ \diagup \quad \diagdown \end{array}$ is unlikely.

It is probably unwise to suggest a reason for the stability of the esters, but it can at least be said that the hydrogen-bonding might be a contributory factor in it.

The infrared spectra were recorded with a Perkin-Elmer spectrophotometer (model 21) with NaCl optics.

1- and 2-Naphthylmethylboronic acids have been tested biologically by Dr. B. Åberg (15) who has reported both to be anti-auxines.

Experimental

Isopropylboronic acid

Isopropylmagnesium bromide, prepared from 12.3 g (0.1 mole) of isopropyl bromide and 2.75 g (0.12 mole) of magnesium, in 110 ml of ether was added with stirring, over a two-hour period, to 24 g (0.11 mole) of tributyl borate (16) in 90 ml of ether at -60° . After standing over night, it was treated with 1M hydrochloric acid, the organic portion separated, and the aqueous phase extracted with ether. The combined ether layers were extracted with 1M sodium hydroxide. The aqueous layer was acidified with hydrochloric acid, precipitating 5.1 g of the crude moist acid. A small sample was carefully recrystallized from water and dried over 65% sulfuric acid, in a desiccator filled with nitrogen. Colourless plates with m.p. $112^\circ\text{--}115^\circ\text{C}$ were obtained. Yield 50–55%.

Anal. Subst. 26.90 mg: 40.10 mg of CO_2 ; 25.20 mg of H_2O .

$\text{C}_3\text{H}_5\text{O}_2\text{B}$ (87.93) Calcd. C 40.98% H 10.3%.

Found C 40.56% H 10.5%.

Diethanolamine ester of isopropylboronic acid

Isopropylboronic acid (4.4 g), diethanolamine (5 g) and 100 ml of benzene were distilled until the water azeotrope was removed. After cooling, the precipitate was collected and crystallized from acetone. Small colourless needles with m. p. 196°–198°C were obtained (4.5 g). Yield 58 %.

All diethanolamine esters mentioned above (Table 1), except these of the naphthylmethylboronic acids, were prepared in the same way.

n-Butylboronic acid from the lithium reagent

To a solution of 21.6 g of tributyl borate in 125 ml of ether, maintained at -60°, was added in a slow stream, over a period of two hours, 62.5 ml of 1.6*M* butyllithium (17). The solution was stirred, and the reaction was held under nitrogen. It was allowed to stand over night and then treated with water and dilute hydrochloric acid. The ethereal layer was extracted with dilute sodium hydroxide, the water layer acidified, and the boronic acid collected; after crystallization from water and drying in a nitrogen filled desiccator, with 65 % sulfuric acid, white plates, m. p. 94°–96°C were obtained. Yield 59 %. The acid was identified as the diethanolamine ester. M. p. and mixed m. p. 153°–155°C.

1-Naphthylmethylboronic acid

This acid was prepared, according to the general procedure, from 1-naphthylmethyl chloride (18). The yield was very low (20–25 %), and the reason seems to be a sensitivity to air, and perhaps, "coupling". The acid is strong enough to permit titration with alkali in the presence of mannitol (phenolphthalein). White plates, m. p. 121°–124°C.

Anal. Subst. 11.30 ml: 8.39 ml of 0.0739*M* NaOH.

$C_{11}H_{11}O_2B$ Equiv. wt. Calcd. 186; Found 182.

2-Naphthylmethylboronic acid

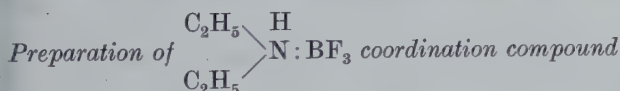
This acid was prepared from 2-naphthylmethyl bromide (19) in the same way as the isomer. Yield 15–20 %. White plates. M. p. 132°–135°C.

Anal. Subst. 10.10 mg: 7.48 ml of 0.0739*M* NaOH.

$C_{11}H_{11}O_2B$ Equiv. wt. Calcd. 186; Found 183.

Diethanolamine esters of naphthylmethylboronic acids

The corresponding boronic acids are very sensitive to air and heat, and azeotropic esterification cannot be used. Instead, the esters are sufficiently insoluble in ether that they can be precipitated directly from this solvent. Thus, to a solution of 2 g of naphthylmethylboronic acid in 10 ml of ether was added with stirring 1 g of diethanolamine, yielding the derivative immediately. Both esters form fine needles from acetone.



A two-necked 100-ml flask fitted with a reflux condenser and a gas inlet tube was immersed in a pail of crushed ice and salt. Diethylamine (3.6 g) in 15 ml of dry chloro-

form was introduced and when the temperature had fallen below 0° , a rapid stream of BF_3 was started through the gas inlet tube, which should drop below the surface of the liquid in the flask. When excess BF_3 was present, as indicated by white fumes at the top of the condenser, the stream of BF_3 was interrupted. Dry nitrogen was passed through the solution for five minutes, in order to remove excess BF_3 and the flask then contains a quantitative yield of a slurry of the coordination compound. It was filtered off and washed many times with dry ether. Small plates with m.p. 166° – 168°C . Kraus and Brown (14) reported the melting point to be in the neighbourhood of 160° .



The preparation was made from dipropylamine in the same way as described above. White, small plates. M.p. 242° – 244°C . Yield: quantitative.

Anal. Subst. 21.40 mg. 33.22 mg of CO_2 ; 17.81 mg of H_2O .

$\text{C}_6\text{H}_{15}\text{F}_3\text{NB}$ (169.0) Calcd. C 42.64 % H 8.95 %.

Found C 42.29 % H 9.31 %.

Piperidine: BF_3 coordination compound

The compound was prepared according to the general procedure. In this case, the compound was not precipitated since it was soluble in chloroform. After removing the solvent, an oily residue was obtained. Crystallization from water gave white plates, m.p. 71° – 73°C . Yield 61 %.

Anal. Subst. 18.70 mg. 26.70 mg of CO_2 ; 12.20 mg of H_2O .

$\text{C}_5\text{H}_{11}\text{F}_3\text{NB}$ (152.97) Calcd. C 39.26 % H 7.25 %.

Found C 38.91 % H 7.30 %.

Summary

Isopropyl-, 1- and 2-naphthylmethylboronic acids and twelve diethanolamine esters of aliphatic boronic acids have been prepared and the corresponding infrared absorption curves investigated. The stability of diethanolamine esters of alkylboronic acids is discussed. Two acids of auxin-type have been tested biologically.

ACKNOWLEDGEMENTS

The author is indebted to Professor A. Fredga for his kind interest. The IR absorption curves were recorded by Dr. Andreas Rosenberg with technical assistance of Mr. S. Bergwall.

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Department of Organic Chemistry, Chemical Institute, University of Uppsala, March 1956.

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Attempted syntheses of indole-2-acetic acid

By MAGNUS MATELL

After the discovery of the growth-regulating properties of indole-3-acetic acid in 1934 (1) a great number of indole compounds have been studied in order to establish structural requirements for auxin activity (2, 3, 4). In that connection indole-2-acetic acid should be of great interest. However, this acid does not seem to have been described in the literature, which may be due to preparative difficulties. The experiments described in this paper were undertaken in order to synthesize indole-2-acetic acid, but this aim was not reached as this investigation was interrupted.

The first attempt to prepare indole-2-acetic acid from 2-hydroxymethylindole via the halomethyl compound and the nitrile was unsuccessful as 2-hydroxymethylindole decomposes rapidly when treated with thionyl chloride or phosphorus halides.

Lengthening the side-chain of indole-2-carboxylic acid according to Arndt-Eistert should be a straightforward way to the desired indole-2-acetic acid. The starting material, indole-2-carboxylic acid, was prepared by reduction of *o*-nitrophenylpyruvic acid obtained by condensation of *o*-nitrotoluene and diethyl oxalate according to known procedures (5, 6). The acid chloride could not be prepared in a state of purity as it decomposes spontaneously even *in vacuo* at room temperature. Its identity was established by conversion to indole-2-carboxamide, which was also prepared from the methyl ester and methanolic ammonia. When treated with diazomethane the acid chloride gave indole-2-diazoketone. At this stage the investigation was interrupted and therefore only a few preliminary experiments on the rearrangement of the diazoketone could be performed. When treated with ethanol and silver oxide or with aqueous silver nitrate according to standard procedures (7) dark-coloured tars were obtained. In another experiment ammonia was passed into an ethanolic solution of indole-2-diazoketone with silver oxide as catalyst. A dark-coloured, crystalline product was isolated but the quantity was too small to permit purification, analysis and identification.

Experimental

o-Nitrophenylpyruvic acid.—The procedure given by Reissert (5) was followed. Yield 40–60 %. After recrystallization from benzene it melted at 116–120° in accordance with Reissert (115–121°).

Indole-2-carboxylic acid.—*o*-Nitrophenylpyruvic acid was reduced according to Kermack *et al.* (6). Yield 65–75 %. The crude acid was recrystallized from formic acid. M.p. 204–206°, which is slightly higher than the value given by Kermack *et al.*

2-Hydroxymethylindole.—To a slurry of LiAlH_4 (2.28 g, 0.06 mole) in dry ether (140 ml) was added a solution of indole-2-carboxylic acid (6.44 g, 0.04 mole) in dry

ether (100 ml). After refluxing for 3 hours 10 % sulphuric acid (90 ml) was carefully added, the ether layer separated and the aqueous solution extracted with four portions of ether. The combined ether extracts were washed with water, sodium bicarbonate solution and water, dried with anhydrous sodium sulphate and evaporated. The residue (5.45 g, 92.5 % of theory) melted at 68–73°. It was recrystallized several times from benzene–petroleum ether. M.p. 73–75°.

Indole-2-diazoketone.—Indole-2-carboxylic chloride was prepared according to Kermack *et al.* (6). The crude chloride was extracted with cold ether. The residue melted at about 110° with decomposition from about 100°. It is unstable and can not be stored. Indole-2-carboxylic chloride (3.6 g, 0.02 mole) in dry ether (75 ml) was slowly added to a solution of diazomethane (2.5 g, 0.06 mole) in dry ether (200 ml). The solution was allowed to stand for 20 hours. The diazoketone separated as large, yellow crystals. The ether was evaporated yielding another crop of yellow crystals. The product can be purified by recrystallization from benzene, benzene–petroleum ether or methanol. It has no sharp melting point but decomposes, slowly at 150°, vigorously at 175°. Yield 3.4 g (92 % of theory).

$C_{10}H_7ON_3$ (185.2) calc.: C 64.86 H 3.81 N 22.69 %
found: C 64.67 H 3.76 N 22.16 %

Methyl indole-2-carboxylate.—Indole-2-carboxylic acid and diazomethane in ether gave the methyl ester in 100 % yield, m.p. 148–152.5°. It was recrystallized from benzene. M.p. 151.5–152.5° (151–152° according to ref. (8)).

Indole-2-carboxamide.—From the methyl ester: Methyl indole-2-carboxylate (1.75 g, 0.01 mole) was mixed with 5 ml of ethanol saturated with ammonia at 0°. The mixture was left at room temperature in a pressure bottle for 2 days. The solution was decanted from the crystals which were reacted with a new portion of methanolic ammonia for 2 days. After repeating the procedure once more all the crystals had disappeared. The combined methanolic solutions gave a residue (1.5 g) which melted at 150–235°. Extraction with hot benzene gave a residue with m.p. 232–233.5°. It was recrystallized from formic acid yielding 1 g of colourless crystals with m.p. 232–234°.

$C_9H_8ON_2$ (160.2) calc.: C 67.48 H 5.04 N 17.49 %
found: C 66.98 H 5.31 N 17.60 %

From the acid chloride: Indole-2-carboxylic chloride was shaken with conc. aqueous ammonia. The crystals were recrystallized from formic acid, m.p. 232–233.5°. When mixed with the amide prepared from the methyl ester the melting point was not depressed.

Summary

Indole-2-diazoketone has been synthesized as a possible intermediate in the preparation of indole-2-acetic acid.

The major part of this work was carried out at the Laboratory of Organic Chemistry, Royal Agricultural College, Uppsala. The author is much obliged to the head of this laboratory, Prof. N. Hellström, for the good experimental resources put at his disposal. Thanks are due to Dr. A. Bernhardt for carrying out the micro analyses. Part of the expenses involved have been defrayed by a grant from *Jordbrukets Forskningsråd*, which is gratefully acknowledged.

Research Laboratory, Mo & Domsjö AB, Örnsköldsvik, April 1956.

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The crystal structure of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$

By GEORG LUNDGREN

With 9 figures in the text

Three years ago the crystal structure of $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ was determined (1). The positions of the uranium atoms were then deduced from Patterson projections but, because of the large X-ray scattering power of uranium, the parameters of the light atoms (sulphur and oxygen) had to be found using geometrical arguments.

Later on, when the structure determination of $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ had been published, the isomorphous cerium compound was obtained (2). Now, the X-ray scattering power of cerium does not completely dominate over that of sulphur and oxygen. It should then be possible to determine the arrangement of the light atoms in $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ directly from the X-ray diffraction data using Fourier methods and in this way it should be possible to check the geometrically determined structure of $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$.

Preparation of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$

The crystals of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ were obtained as a by-product during the preparation of $\text{CeOSO}_4\text{H}_2\text{O}$ (2): A solution of cerium sulphate (The British Drug Houses Ltd., low in other rare earths) in 1M sulphuric acid was sealed in a glass tube and heated to 200°C for some days, after which a precipitate formed. When the tube had been cooled, the precipitate was filtered off and dried in air. It generally consisted of yellow crystals of $\text{CeOSO}_4\text{H}_2\text{O}$, contaminated with a whitish yellow crystalline powder consisting of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$. Sometimes the yield of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ was increased so that 50–75 % of the precipitate consisted of this phase. This happened especially when the heating time was rather short and the volume of solution heated rather small (about 10 ml).

The crystals of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ obtained were small, very light yellow octahedra.

Since the crystals could not be obtained free from other phases, they were not analyzed quantitatively. There is however little doubt as to their formula since a small, specially selected sample of them gave a powder photograph that was almost identical with that of $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ (ref. (1)) if a small shift in the positions of the powder lines was disregarded.

Unit cell and space group

From powder photographs, taken with CuK radiation in focusing cameras of Phragmén type, the cell dimensions of the tetragonal unit cell were calculated (cf. Table 1) and compared with those of $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$:

G. LUNDGREN, *The crystal structure of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$*

	$\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$	$\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$
a	$10.661 \pm 0.005 \text{ \AA}$	$10.741 \pm 0.005 \text{ \AA}$
c	$10.288 \pm 0.005 \text{ \AA}$	$10.377 \pm 0.005 \text{ \AA}$
V	$1169.3 \text{ \AA}^3$	$1197.2 \text{ \AA}^3$
c/a	0.965_0	0.966_1

The cell dimensions were calculated with $\lambda_{\text{Cr K}\alpha_1} = 2.28962 \text{ \AA}$. As is expected from the decrease in ionic radius from uranium to cerium, the unit cell of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ is a little smaller than that of $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$.

Since there are 2 formula units in the unit cell (1), the density calculated for $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ is 4.399.

Rotation and Weissenberg photographs

From one of the samples prepared, it was possible to pick out a crystal that was big enough to give single crystal photographs. It was a very small octahedron, only about 0.05 mm in diameter. With this crystal, rotation and Weissenberg photographs ($hk0 - hk4$; $h0l - h4l$; $hhl - h, h+2, l$) were taken using Cu K radiation. The reflexions were recorded photographically with multiple film technique and their intensities were estimated visually. The F^2 values were then calculated using the polarization and Lorentz' factor given by Lu (3). No correction was applied for the absorption.

The photographs showed the Laue symmetry to be $4/m$ and the only reflexions systematically absent were hkl with $h+k+l = \text{odd}$, which is characteristic of the space groups no. 87 $I4/m$, no. 82 $I\bar{4}$ and no. 79 $I4$.

Positions of the cerium atoms

The arguments used for finding the positions of the heavy atoms in $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ (ref. (1)) are also valid for $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ since the intensities of the reflexions and thus also the Patterson projections (Fig. 1) are rather similar for the two compounds.

The parameters for the cerium atoms as obtained from the Patterson functions should then be:

4 Ce_1 in $I4/m$ 4(e): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (0, 0, z)$ with $z = 0.260$

8 Ce_2 in $I4/m$ 8(h): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, 0; \bar{y}, x, 0)$ with $x = 0.252$, $y = 0.030$

Positions of the sulphur and oxygen atoms

To find out the positions of the sulphur atoms, the electron density projections $\rho(xyp)$ and $\rho(xpz)$ were calculated (for the latter projection presuming the centrosymmetric space group $I4/m$). The signs of the F values could be determined by the cerium contributions for all reflexions except five of the weakest ($10\ 2\ 0$; $1\ 3\ 0$; $2\ 6\ 0$; $2\ 10\ 0$; $8\ 10\ 0$). Maxima of heights corresponding to sulphur atoms were then found at the following positions:

4 S_1 in $I4/m$ 4(d): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (0, \frac{1}{2}, \frac{1}{4})$

8 S_2 in $I4/m$ 8(h): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, 0; \bar{y}, x, 0)$ with $x = 0.283$, $y = 0.378$

Table 1. Powder photographs of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$. Cr K radiation
 $\lambda_{\text{Cr } K\alpha} = 2.2909 \text{ \AA}$.

hkl	$10^4 \sin^2 \theta$ calc	$10^4 \sin^2 \theta$ obs	$pF_{hkl}^2 + pF_{\bar{h}\bar{k}\bar{l}}^2$ calc	$I_{hkl} + I_{\bar{h}\bar{k}\bar{l}}$ obs
220	924	—	8	—
202	958	(950)	245	(st)
310	1154	1152	70 + 24	m ⁺
301	1163		93	
103	1231	1226	31	vw
222	1419	1417	525	st
321	1625	1623	53 + 48	w ⁺
312	1650	(1649)	3 + 185	(m)
213	1693	1689	13 + 23	vw
400	1847	1846	120	w
004	1983	1981	128	w ⁺
330	2078	2078	25	vw
411	2086		46 + 5	
303	2155	(2153)	90	(w)
114	2214	2211	8	vvw
420	2309	2310	56 + 42	w ⁺
402	2343	—	8	—
204	2445	2444	14	vvw
332	2574	2569	26	vw
323	2616	2621	5 + 176	st
422	2805	2807	23 + 46	m
224	2907	(2906)	6	(vvw)
510	3001	3010	74 + 0	st
431	3010		3 + 168	
501	3010		3	
413	3078	3079	189 + 34	st
314	3138	3138	181 + 2	st
105	3214	3212	18	vvw
521	3472	3471	112 + 1	m
512	3497	3505	3 + 81	w
215	3676	(3681)	24 + 90	(w ⁺)
440	3694	3696	165	m
404	3830	3836	470	st
530	3925	3932	0 + 101	w ⁺
433	4002	4001	2 + 152	m
503	4002		18	
334	4061		34	
305	4138	4138	55	vvw
600	4156	—	2	vw
442	4190	—	1	—
424	4292	4295	116 + 133	—
611	4395	4393	4 + 292	m
532	4421	4412	245 + 8	m
006	4463	(4462)	40	(w)
523	4463		31 + 13	
325	4600	4607	44 + 119	w
620	4618	—	4 + 4	—
602	4652	4655	126	w
116	4693	4695	53	vw
541	4857	4859	0 + 102	vw
206	4924	4923	84	vw
514	4985	4979	65 + 13	vw

The horizontal line marks the boundary between the angular ranges of two different focusing cameras used. Reflexions systematically absent in space group $I4/m$ have been omitted. Reflexions coinciding with β reflexions are given in brackets. The powder photographs were measured and interpreted to $\sin^2 \theta = 0.95$.

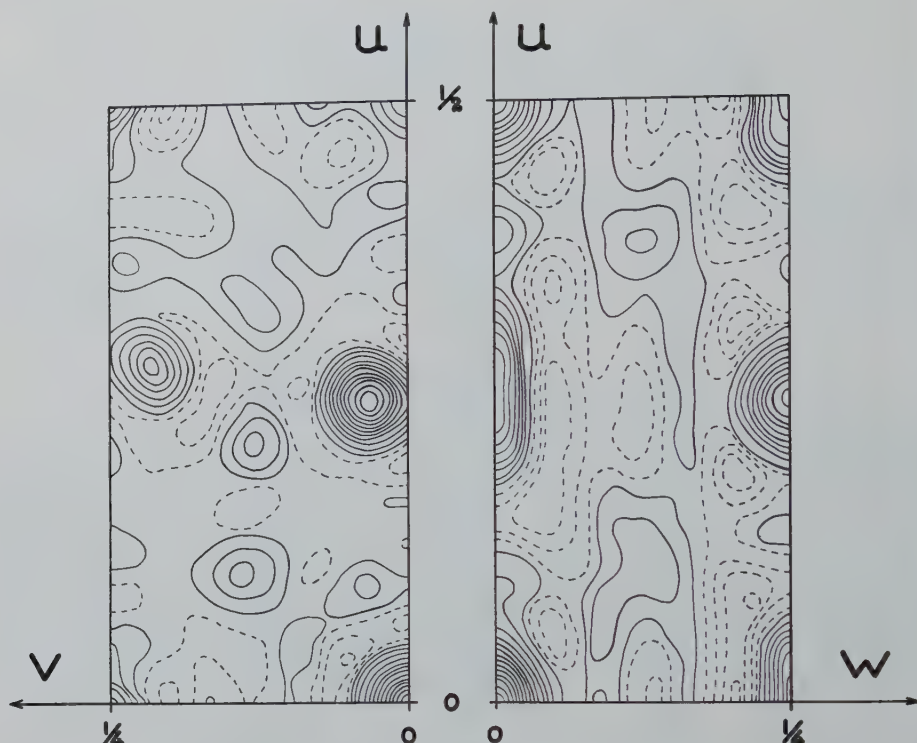


Fig. 1. Patterson projections $P(uvp)$ and $P(upw)$. For the largest maxima, $(0,0)$ in $P(uvp)$ and $(0,0)$, $(\frac{1}{2}, 0)$ and $(\frac{1}{4}, \frac{1}{4})$ in $P(upw)$, only every second contour has been marked. Dashed lines indicate negative values.

With these positions, the signs of the remaining F values could be obtained. $\rho(xyp)$ was then recalculated with all the observed F values. The final electron density projections on the xy and xz planes are shown in Fig. 2. The maxima of the Ce_1 and Ce_2 atoms stand out clearly and are surrounded by small diffraction effects. The positions of the sulphur atoms are also seen in both projections. There are, however, also some weak maxima that could be ascribed to oxygen peaks. The following set of parameters is thus obtained from $\rho(xyp)$ and $\rho(xpz)$ (the indices of the atoms are in agreement with those given for $U_6O_4(OH)_4(SO_4)_6$):

- 4 Ce_1 in $I4/m$ 4(e): $(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (0,0,z)$ with $z=0.256$
- 8 Ce_2 in $I4/m$ 8(h): $(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x,y,0; \bar{y},x,0)$ with $x=0.252$, $y=0.032$
- 4 S_1 in $I4/m$ 4(d): $(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (0, \frac{1}{2}, \frac{1}{4})$
- 8 S_2 in $I4/m$ 8(h): $(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x,y,0; \bar{y},x,0)$ with $x=0.282$, $y=0.376$
- 16 O_1 in $I4/m$ 16(i): $(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x,y,z; \bar{y},x,z; \bar{x},\bar{y},z; y,\bar{x},z)$
with $x=0.10_7$, $y=0.13_1$, $z=0.11_3$
- 16 O_2 in $I4/m$ 16(i): $(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x,y,z; \bar{y},x,z; \bar{x},\bar{y},z; y,\bar{x},z)$
with $x=0.40_7$, $y=0.04_7$, $z=0.16_5(?)$
- 16 O_3 in $I4/m$ 16(i): $(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x,y,z; \bar{y},x,z; \bar{x},\bar{y},z; y,\bar{x},z)$
with $x=0.34_4$, $y=0.43_3$, $z=?$

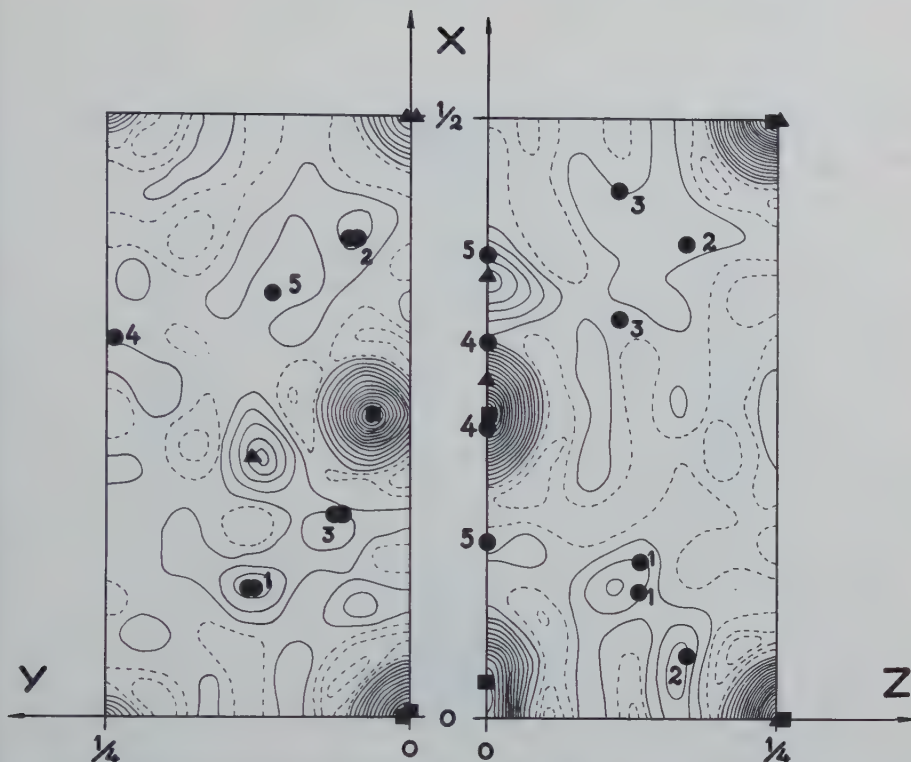


Fig. 2. Electron density projections $\rho(xyp)$ and $\rho(xpz)$. The final positions of the cerium (■), sulphur (▲), and oxygen (●) atoms have been indicated. The figures denote the different oxygen positions. For the cerium maximum at (0, 0) only every second contour has been marked. Dashed lines indicate negative values.

No reliable coordinates could be found for 8 O₄ and 8 O₅.

The positions found for the sulphur atoms are in agreement with the Patterson projections since all the vectors Ce-S (calculated from the parameters given above) are situated at low peaks or in weakly positive regions in $P(uvp)$ and $P(upw)$.

Refinement of the sulphur and oxygen parameters

To get more accurate coordinates for the atoms found in the electron density projections and to find out the positions of the atoms that were not seen there, three-dimensional electron density calculations were performed. At first, $\rho(xy0)$ and $\rho(x0z)$ were calculated using 689 of the 785 reflexions obtainable with Cu K radiation. Among them, 266 were too weak to be found in the Weissenberg photographs. (Their intensities were less than a few tenths of a per cent of the strongest reflexion.) The signs of the F values for the reflexions observed were almost entirely determined by the cerium contributions.

As is expected, $\rho(x0z)$ in Fig. 3 shows only the maxima corresponding to the Ce₁, Ce₂ and S₁ atoms since the S₂ and oxygen atoms are not situated in or close to the

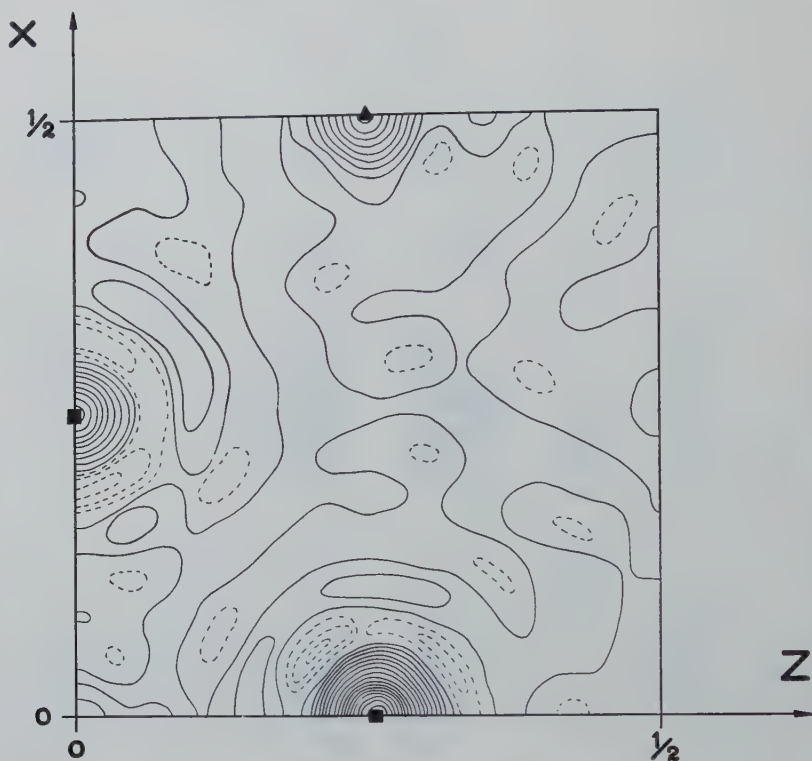


Fig. 3. Electron density section $\rho(x0z)$ showing the positions of the Ce_1 (■), Ce_2 (■) and S_1 (▲) atoms. For the cerium maxima, only every second contour has been marked. Dashed lines indicate negative values.

plane $y=0$. The diffraction effects around the cerium atoms seem to be of the same order of magnitude as in $\rho(xpz)$.

In $\rho(xy0)$ (Fig. 4), the Ce_2 and S_2 atoms are seen but there also appear two maxima that should correspond to oxygen atoms. In $\rho(xyp)$ (Fig. 2), there are only very low maxima rather close to these positions but they correspond rather well to the O_4 and O_5 positions in $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$. The diffraction effects (especially around the cerium atoms) are a little less than those in $\rho(xyp)$ but they are of nearly the same height as the peaks ascribed to the O_4 and O_5 atoms. However, they could not possibly correspond to oxygen atoms since they are situated at positions expected for diffraction effects from the cerium atoms (cf. a paper by Doi (4)), whereas the O_4 and O_5 maxima seem to be real (cf. below).

From $\rho(xy0)$ and $\rho(x0z)$, the following parameters are obtained:

- 4 Ce_1 in $I4/m$ 4(e): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (0, 0, z)$ with $z=0.257$
- 8 Ce_2 in $I4/m$ 8(h): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, 0; \bar{y}, x, 0)$ with $x=0.252$, $y=0.032$
- 4 S_1 in $I4/m$ 4(d): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (0, \frac{1}{2}, \frac{1}{4})$
- 8 S_2 in $I4/m$ 8(h): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, 0; \bar{y}, x, 0)$ with $x=0.283$, $y=0.370$
- 8 O_4 in $I4/m$ 8(h): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, 0; \bar{y}, x, 0)$ with $x=0.315$, $y=0.240$
- 8 O_5 in $I4/m$ 8(h): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, 0; \bar{y}, x, 0)$ with $x=0.155$, $y=0.403$

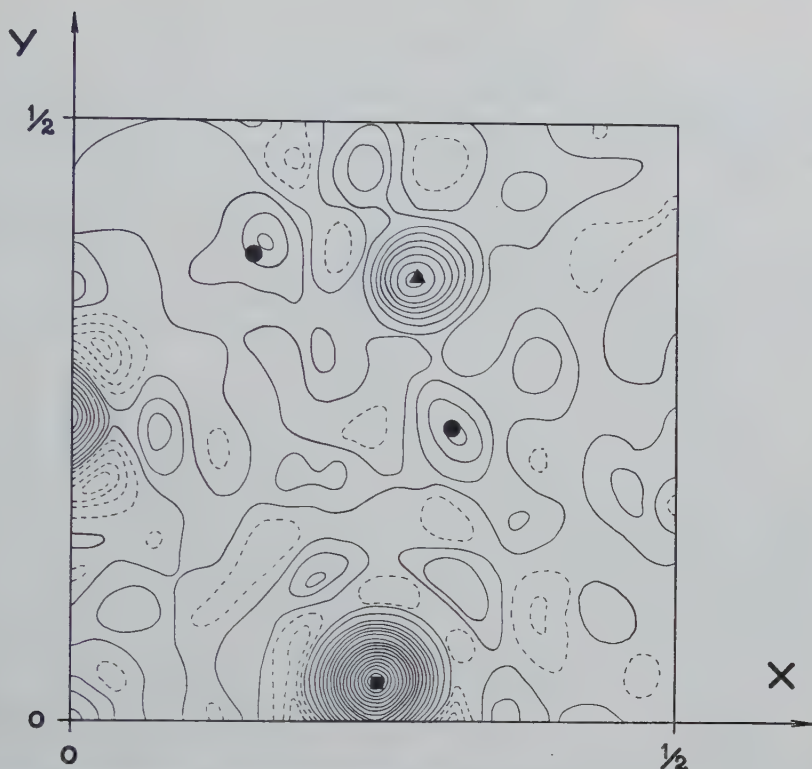


Fig. 4. Electron density section $\rho(xy0)$ showing the positions of the Ce_2 ($\blacksquare$), S_2 ($\blacktriangle$), O_4 ($\bullet$) and O_5 ($\bullet$) atoms. For the cerium maximum, only every second contour has been marked. Dashed lines indicate negative values.

To improve the parameters of the S_2 , O_4 and O_5 atoms, first the cerium and then also the sulphur atoms were subtracted from $\rho(xy0)$. In this way, most of the diffraction effects from the heavy atoms should disappear from $\rho(xy0)$ and more reliable sulphur and oxygen coordinates should be obtained. The temperature factor that should have been introduced in these calculations was found to be negligible when calculated with the ordinary procedure. Probably it approximately cancels out with the absorption effect.

The results are given in Fig. 5 ($\rho'(xy0)$ with the cerium atoms subtracted) and in Fig. 6 ($\rho''(xy0)$ with the cerium and sulphur atoms subtracted). As was expected, most of the diffraction effects have been reduced or have disappeared but the maxima ascribed to the light atoms are of about the same height as before. There remains only one false peak of the same height as the oxygen atoms. It is, however, situated so close to S_2 (1.1 Å) that it could not possibly correspond to an oxygen atom. The parameters of the S_2 , O_4 , and O_5 atoms should then be:

$$\begin{array}{l} \text{From } \rho'(xy0) \quad \left\{ \begin{array}{l} 8 \text{ S}_2 \text{ in } I4/m \text{ 8(h) with } x=0.283, y=0.369 \\ 8 \text{ O}_4 \text{ in } I4/m \text{ 8(h) with } x=0.311, y=0.249 \\ 8 \text{ O}_5 \text{ in } I4/m \text{ 8(h) with } x=0.151, y=0.385 \end{array} \right. \\ \text{From } \rho''(xy0) \quad \left\{ \begin{array}{l} 8 \text{ O}_4 \text{ in } I4/m \text{ 8(h) with } x=0.312, y=0.247 \\ 8 \text{ O}_5 \text{ in } I4/m \text{ 8(h) with } x=0.148, y=0.382 \end{array} \right. \end{array}$$

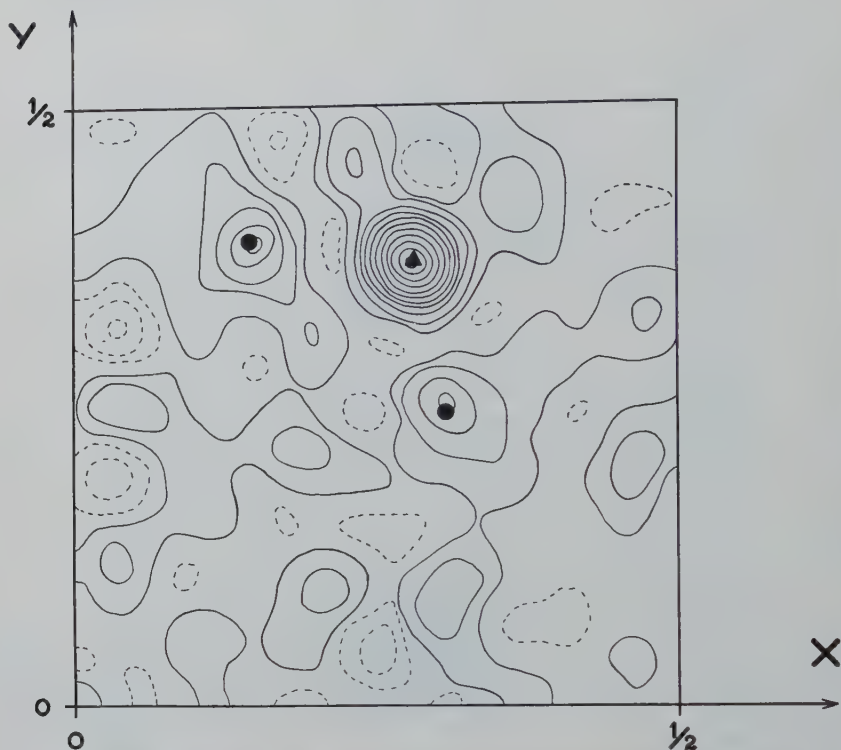


Fig. 5. Electron density section $\rho'(xy0)$ with the cerium atoms (Ce_1 and Ce_2) subtracted. The positions of the S_2 ($\blacktriangle$), O_4 ($\bullet$) and O_5 ($\bullet$) atoms are shown. Dashed lines indicate negative values.

In $\rho(xyp)$ and $\rho(xpz)$ there also appeared peaks corresponding to 16-fold oxygen positions (O_1 , O_2 and O_3). To get more accurate parameters for them, electron density sections through the unit cell were calculated in the following order (the Ce and S atoms were subtracted):

- $\rho''(0.107, y, z)$ to obtain the y and z parameters of O_1 , by which also O_2 and O_5 appeared
- $\rho''(x, y, 0.131)$ to obtain the x and y parameters of O_1 , by which also O_2 and O_3 appeared
- $\rho''(x, y, 0.170)$ to obtain the x and y parameters of O_2 , by which also O_1 appeared
- $\rho''(0.332, y, z)$ to obtain the y and z parameters of O_3 , by which also O_4 and O_5 appeared
- $\rho''(x, y, 0.117)$ to obtain the x and y parameters of O_3 , by which also O_1 appeared

The results are shown in Figs. 7 and 8. As is seen, the diffraction effects are rather low and the parameters for O_1 – O_3 should be:

- 16 O_1 in $I4/m\ 16(i)$ with $x=0.106$, $y=0.132$, $z=0.131$
- 16 O_2 in $I4/m\ 16(i)$ with $x=0.398$, $y=0.052$, $z=0.171$
- 16 O_3 in $I4/m\ 16(i)$ with $x=0.332$, $y=0.439$, $z=0.112$

Final parameters of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$

The following structure is thus proposed for $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ (the figures in brackets give the parameters obtained for the geometrically determined structure of $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ (the hydrogen atoms are assumed to be situated as in the uranium compound, i.e. 16 O_1 consists of 8 $\text{O} + 8 \text{OH}$):

Space group: no. 87 $I4/m$. 2 formula units in the unit cell.

Atomic parameters:

Atoms	Point position	Parameters			The parameters were obtained from
		x	y	z	
Ce_1	4 (e)	0	0	0.257 (0.260)	$Q(x, 0, z)$
Ce_2	8 (h)	0.252 (0.252)	0.032 (0.030)	0	$Q(x, y, 0)$
S_1	4 (d)	0	$\frac{1}{2}$	$\frac{1}{4}$	
S_2	8 (h)	0.283 (0.27 ₂)	0.369 (0.37 ₉)	0	$Q''(x, y, 0)$
O_1	16 (i)	0.106 (0.11 ₃)	0.132 (0.14 ₄)	0.131 (0.13 ₃)	$Q''(x, y, 0.131)$ and $Q''(0.107, y, z)$
O_2	16 (i)	0.398 (0.40 ₀)	0.052 (0.05 ₃)	0.171 (0.16 ₈)	$Q''(x, y, 0.170)$ and $Q''(0.107, y, z)$
O_3	16 (i)	0.332 (0.32 ₆)	0.438 (0.43 ₇)	0.113 (0.11 ₆)	$Q''(x, y, 0.117)$ and $Q''(0.332, y, z)$
O_4	8 (h)	0.312 (0.30 ₀)	0.243 (0.24 ₄)	0	$Q''(x, y, 0)$ and $Q''(0.332, y, z)$
O_5	8 (h)	0.148 (0.13 ₅)	0.386 (0.39 ₈)	0	$Q''(x, y, 0)$, $Q''(0.332, y, z)$ and $Q''(0.107, y, z)$

$$(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm$$

$$4 \text{ (d)} (0, \frac{1}{2}, \frac{1}{4}) \quad 8 \text{ (h)} (x, y, 0; \bar{y}, x, 0)$$

$$4 \text{ (e)} (0, 0, z) \quad 16 \text{ (i)} (x, y, z; \bar{y}, x, z; \bar{x}, \bar{y}, z; y, \bar{x}, z)$$

The accuracy of the parameters is estimated to be ± 0.002 for Ce, ± 0.003 for S and ± 0.005 for O.

Using these parameters, the F values were calculated for the reflexions and compared with the observed ones. They are given in Table 2 for $hk0$, $h0l$, hkl and $h1l$. Table 3 gives the details for some reflexions which have high sulphur and oxygen contributions to the intensities. As is seen, there is a rather good agreement between the observed and calculated data. The reliability index R calculated according to Booth (5) was found to be 0.17 for $hk0$ and 0.19 for $h0l$ (absent reflexions included) or 0.10 for $hk0$ and 0.13 for $h0l$ (absent reflexions not included), showing that the structure should be essentially correct as regards the heavy atoms.

Discussion of the structure

The structure of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ is shown in Fig. 9. It is built up of isolated $\text{Ce}_6\text{O}_4(\text{OH})_4^{12+}$ complexes and sulphate groups as described in the paper on $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ (ref. (1)). The arrangement is quite different from that of $\text{CeOSO}_4 \cdot \text{H}_2\text{O}$ (2), which contains infinite chainlike complexes $(\text{CeO})_n^{2n+}$.

The agreement between the parameters obtained for $\text{U}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ (ref. (1)) and those given in this paper for $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ is very good, the maximum deviation being 0.20 Å in the positions of the oxygen atoms. The results obtained during the geometrical structure determination of the former compound are thus confirmed.

Table 2. Calculated and observed structure factors from Weissenberg photographs of $Ce_6O_4(OH)_4(SO_4)_6$.

$h k l$	F calc	F obs	$h k l$	F calc	F obs	$h k l$	F calc	F obs	$h k l$	F calc	F obs
2 0 0	57	57	2 8 0	64	69	1 4 1	14	16	8 0 2	2	—
4 0 0	98	94	4 8 0	78	87	3 4 1	82	87	10 0 2	-83	94
6 0 0	12	—	6 8 0	74	80	5 4 1	-4	—	12 0 2	-35	34
8 0 0	93	95	8 8 0	37	39	7 4 1	19	—	1 0 3	25	29
10 0 0	-9	—	10 8 0	21	21	9 4 1	-20	—	3 0 3	60	51
12 0 0	29	25	1 9 0	-17	—	11 4 1	2	—	5 0 3	27	18
1 1 0	45	46	3 9 0	60	58	2 5 1	6	—	7 0 3	15	—
3 1 0	75	77	5 9 0	1	—	4 5 1	64	70	9 0 3	-20	—
5 1 0	77	77	7 9 0	90	95	6 5 1	15	—	11 0 3	6	—
7 1 0	77	71	9 9 0	46	36	8 5 1	35	45	0 0 4	143	115
9 1 0	65	71	2 10 0	28	42	10 5 1	4	—	2 0 4	24	16
11 1 0	50	59	4 10 0	-7	—	12 5 1	40	43	4 0 4	137	135
13 1 0	18	—	6 10 0	26	—	1 6 1	-108	120	6 0 4	23	24
2 2 0	-26	23	8 10 0	36	25	3 6 1	-4	—	8 0 4	77	83
4 2 0	67	72	1 11 0	0	—	5 6 1	-48	53	10 0 4	-4	—
6 2 0	-17	17	3 11 0	41	35	7 6 1	38	45	12 0 4	32	21
8 2 0	82	94	5 11 0	-34	31	9 6 1	-32	—	1 0 5	27	17
10 2 0	25	19	7 11 0	19	21	11 6 1	41	42	3 0 5	47	41
12 2 0	82	91	2 12 0	94	88	2 7 1	-20	—	5 0 5	14	14
1 3 0	-44	55	4 12 0	34	30	4 7 1	-39	45	7 0 5	-2	—
3 3 0	45	57	6 12 0	65	78	6 7 1	-40	43	9 0 5	-46	37
5 3 0	-3	—	1 13 0	23	—	8 7 1	-18	—	11 0 5	-14	—
7 3 0	35	48	3 13 0	50	40	10 7 1	-34	40	0 0 6	80	65
9 3 0	-40	39	1 0 1	36	35	1 8 1	15	—	2 0 6	-58	58
11 3 0	20	—	3 0 1	61	64	3 8 1	60	72	4 0 6	9	—
13 3 0	-15	—	5 0 1	10	—	5 8 1	-31	34	6 0 6	-71	56
2 4 0	58	70	7 0 1	17	—	7 8 1	44	56	8 0 6	2	—
4 4 0	115	115	9 0 1	-18	—	9 8 1	-38	47	10 0 6	-72	65
6 4 0	37	40	11 0 1	-13	—	2 9 1	16	—	1 0 7	46	47
8 4 0	46	59	13 0 1	-28	21	4 9 1	7	—	3 0 7	51	58
10 4 0	17	—	2 1 1	-34	33	6 9 1	45	48	5 0 7	18	29
12 4 0	46	41	4 1 1	43	40	8 9 1	6	—	7 0 7	23	—
1 5 0	1	—	6 1 1	12	—	1 10 1	-49	69	9 0 7	-8	—
3 5 0	90	94	8 1 1	74	74	3 10 1	-16	—	0 0 8	151	129
5 5 0	21	—	10 1 1	4	—	5 10 1	-32	42	2 0 8	22	13
7 5 0	85	99	12 1 1	44	53	7 10 1	13	—	4 0 8	80	89
9 5 0	20	30	1 2 1	-50	46	2 11 1	-3	—	6 0 8	18	—
11 5 0	74	86	3 2 1	-46	50	4 11 1	-30	25	8 0 8	75	60
2 6 0	18	14	5 2 1	-67	69	6 11 1	9	—	10 0 8	-9	—
4 6 0	52	43	7 2 1	16	—	1 12 1	7	—	1 0 9	6	—
6 6 0	5	—	9 2 1	-8	—	3 12 1	43	48	3 0 9	22	—
8 6 0	29	27	11 2 1	27	—	5 12 1	-5	—	5 0 9	-6	—
10 6 0	53	58	13 2 1	-1	—	2 13 1	29	36	7 0 9	-13	—
12 6 0	62	63	2 3 1	-44	45	4 13 1	0	—	9 0 9	-14	—
1 7 0	-7	—	4 3 1	10	—	0 0 2	83	63	0 0 10	51	37
3 7 0	43	40	6 3 1	-78	76	2 0 2	-99	95	2 0 10	-49	54
5 7 0	-26	25	8 3 1	-11	—	4 0 2	18	—	4 0 10	15	—
7 7 0	5	—	10 3 1	-50	54	6 0 2	-71	74	6 0 10	-45	48
9 7 0	-33	45	12 3 1	-11	—				8 0 10	1	—
11 7 0	25	24									

Table 2 (continued)

$h k l$	F calc	F obs	$h k l$	F calc	F obs	$h k l$	F calc	F obs	$h k l$	F calc	F obs
1 0 11	30	42	$\bar{8}$ 1 3	2	—	5 1 6	-1	—	2 1 9	-33	52
3 0 11	55	53	$\bar{10}$ 1 3	-56	60	7 1 6	11	—	4 1 9	26	31
5 0 11	32	28	$\bar{12}$ 1 3	15	—	9 1 6	18	—	6 1 9	-1	—
0 0 12	102	112				11 1 6	5	—	8 1 9	40	36
2 0 12	22	23	1 1 4	18	13	$\bar{3}$ 1 6	-67	69	2 1 9	-36	50
4 0 12	77	80	3 1 4	85	83	$\bar{5}$ 1 6	-39	30	4 1 9	12	—
1 1 2	-31	22	5 1 4	51	47	$\bar{7}$ 1 6	-56	63	6 1 9	-79	83
3 1 2	11	8	7 1 4	43	51	$\bar{9}$ 1 6	-62	56	8 1 9	-6	—
5 1 2	-10	—	9 1 4	59	60	$\bar{11}$ 1 6	-45	37			
7 1 2	-7	—	11 1 4	60	60				1 1 10	-18	—
9 1 2	10	—	$\bar{3}$ 1 4	9	—	2 1 7	-10	—	3 1 10	9	—
11 1 2	8	—	5 1 4	22	—	4 1 7	50	59	5 1 10	2	—
13 1 2	-16	—	7 1 4	-10	—	6 1 7	25	37	7 1 10	2	—
$\bar{3}$ 1 2	-86	75	$\bar{9}$ 1 4	-12	—	8 1 7	65	71	$\bar{5}$ 1 10	-55	57
$\bar{5}$ 1 2	-57	56	$\bar{11}$ 1 4	-9	—	10 1 7	10	—	5 1 10	-34	43
7 1 2	-66	68				$\bar{2}$ 1 7	-25	—	7 1 10	-49	48
$\bar{9}$ 1 2	-62	66	2 1 5	-31	33	4 1 7	16	23			
$\bar{11}$ 1 2	-50	59	4 1 5	59	47	$\bar{6}$ 1 7	-72	66	2 1 11	-2	—
$\bar{13}$ 1 2	-34	33	6 1 5	19	27	$\bar{8}$ 1 7	19	—	4 1 11	59	58
			8 1 5	38	41	10 1 7	-38	34	6 1 11	27	22
2 1 3	-23	11	10 1 5	-11	—	1 1 8	39	22	$\bar{2}$ 1 11	-19	12
4 1 3	87	85	12 1 5	46	39	3 1 8	49	63	4 1 11	21	19
6 1 3	33	21	$\bar{2}$ 1 5	-60	56	5 1 8	36	41	6 1 11	-55	45
8 1 3	43	43	4 1 5	-11	—	7 1 8	45	48			
10 1 3	-12	—	6 1 5	-99	97	9 1 8	52	48	1 1 12	11	11
12 1 3	55	52	$\bar{8}$ 1 5	-1	—	$\bar{3}$ 1 8	-20	19	3 1 12	46	33
$\bar{2}$ 1 3	-30	27	10 1 5	-54	59	5 1 8	1	—	$\bar{5}$ 1 12	-7	—
4 1 3	37	30	1 1 6	-46	45	7 1 8	-8	—			
6 1 3	-85	77	3 1 6	5	—	9 1 8	-6	—			

The distances between neighbouring atoms in $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ are as follows:

$\text{Ce}_1\text{--}4\text{Ce}_2$; $\text{Ce}_2\text{--}2\text{Ce}_1 = 3.78 \text{ \AA}$
 $\text{Ce}_2\text{--}2\text{Ce}_2 = 3.83 \text{ \AA}$
 $\text{Ce}_1\text{--}4\text{O}_1$; $\text{O}_1\text{--}\text{Ce}_1 = 2.22 \text{ \AA}$
 $\text{Ce}_2\text{--}4\text{O}_1$; $\text{O}_1\text{--}2\text{Ce}_2 = 2 \times 2.32$; $2 \times 2.37 \text{ \AA}$
 $\text{Ce}_1\text{--}4\text{O}_3$; $\text{O}_3\text{--}\text{Ce}_1 = 2.33 \text{ \AA}$
 $\text{Ce}_2\text{--}2\text{O}_2$; $\text{O}_2\text{--}\text{Ce}_2 = 2.36 \text{ \AA}$
 $\text{Ce}_2\text{--}\text{O}_4$; $\text{O}_4\text{--}\text{Ce}_2 = 2.34 \text{ \AA}$
 $\text{Ce}_2\text{--}\text{O}_5$; $\text{O}_5\text{--}\text{Ce}_2 = 2.39 \text{ \AA}$
 $\text{S}_1\text{--}4\text{O}_3$; $\text{O}_3\text{--}\text{S}_1 = 1.47 \text{ \AA}$
 $\text{S}_2\text{--}2\text{O}_3$; $\text{O}_3\text{--}\text{S}_2 = 1.47 \text{ \AA}$
 $\text{S}_2\text{--}\text{O}_4$; $\text{O}_4\text{--}\text{S}_2 = 1.38 \text{ \AA}$
 $\text{S}_2\text{--}\text{O}_5$; $\text{O}_5\text{--}\text{S}_2 = 1.45 \text{ \AA}$

$\text{O}_1\text{--}2\text{O}_2$; $\text{O}_2\text{--}2\text{O}_1 = 3.25$; $3.32 \text{ \AA}$
 $\text{O}_1\text{--}2\text{O}_3$; $\text{O}_3\text{--}2\text{O}_1 = 2.82$; $3.21 \text{ \AA}$
 $\text{O}_1\text{--}\text{O}_4$; $\text{O}_4\text{--}2\text{O}_1 = 2.84 \text{ \AA}$
 $\text{O}_1\text{--}\text{O}_5$; $\text{O}_5\text{--}\text{O}_1 = 3.06 \text{ \AA}$
 $\text{O}_2\text{--}3\text{O}_2 = 2.44^*$; $2 \times 2.37^* \text{ \AA}$
 $\text{O}_2\text{--}\text{O}_3$; $\text{O}_3\text{--}\text{O}_2 = 3.31 \text{ \AA}$
 $\text{O}_2\text{--}\text{O}_4$; $\text{O}_4\text{--}2\text{O}_2 = 2.84 \text{ \AA}$
 $\text{O}_2\text{--}2\text{O}_5$; $\text{O}_5\text{--}4\text{O}_2 = 2.77$; $3.07 \text{ \AA}$
 $\text{O}_3\text{--}3\text{O}_3 = 2.33^*$; $2 \times 2.70 \text{ \AA}$
 $\text{O}_3\text{--}2\text{O}_4$; $\text{O}_4\text{--}4\text{O}_3 = 2.39^*$; $3.06 \text{ \AA}$
 $\text{O}_3\text{--}\text{O}_5$; $\text{O}_5\text{--}2\text{O}_3 = 2.35^* \text{ \AA}$
 $\text{O}_4\text{--}2\text{O}_5$; $\text{O}_5\text{--}2\text{O}_4 = 2.32^*$; $3.38 \text{ \AA}$

O—O distances within a sulphate group have been marked with an asterisk.

Table 3. Calculated and observed structure factors from Weissenberg photographs of $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$. Reflexions with high sulphur and oxygen contributions.

hkl	F_{Ce} calc	F_{S} calc	F_{O} calc	F_{tot} calc	F_{obs}	hkl	F_{Ce} calc	F_{S} calc	F_{O} calc	F_{tot} calc	F_{obs}
4 0 0	127	8	-37	98	94	2 0 2	-55	-25	-19	-99	95
8 0 0	70	15	8	93	95	12 0 2	-21	-17	3	-35	34
5 1 0	70	-17	24	77	77	0 0 4	140	33	-30	143	115
7 1 0	87	-16	6	77	71	2 0 4	41	0	-17	24	16
4 2 0	55	27	-15	67	72	4 0 4	113	6	18	137	135
12 2 0	73	15	-6	82	91	9 0 5	-18	-10	-18	-46	37
1 3 0	13	-34	-23	-44	55	0 0 6	42	9	29	80	65
5 3 0	-18	-9	24	-3	—	2 0 6	-42	-17	1	-58	58
9 3 0	-21	-19	0	-40	39	12 0 6	19	-16	-4	-1	—
4 4 0	101	-3	17	115	115	0 0 8	102	24	25	151	129
6 4 0	29	20	-12	37	40	0 0 12	80	19	3	102	112
8 4 0	55	10	-19	46	59	1 1 2	-54	17	6	-31	22
10 4 0	1	-2	18	17	—	3 1 2	-15	19	7	11	8
1 5 0	12	6	-17	1	—	7 1 2	10	1	-18	-7	—
3 5 0	100	-16	6	90	94	9 1 2	-11	21	0	10	—
5 5 0	36	-17	2	21	—	5 1 2	-74	25	-8	-57	56
2 6 0	-12	19	11	18	14	6 1 3	4	16	13	33	21
4 6 0	21	5	26	52	43	8 1 3	72	-9	-20	43	43
10 6 0	32	19	2	53	58	2 1 3	-60	15	15	-30	27
7 7 0	33	-20	-8	5	—	4 1 3	17	2	18	37	30
4 8 0	56	16	6	78	87	1 1 4	44	-8	-18	18	13
6 8 0	49	10	15	74	80	3 1 4	73	-3	15	85	83
9 9 0	29	-1	18	46	36	5 1 4	63	-15	3	51	47
8 10 0	11	16	9	36	25	7 1 4	79	-15	-21	43	51
3 0 1	41	17	3	61	64	3 1 4	10	-27	26	9	—
4 1 1	77	-7	-27	43	40	6 1 5	-9	15	13	19	27
6 1 1	-3	17	-2	12	—	1 1 6	-40	11	-17	-46	45
8 1 1	68	-9	15	74	74	9 1 6	-9	19	8	18	—
1 2 1	-75	17	8	-50	46	5 1 6	-60	21	0	-39	30
3 2 1	-22	-21	-3	-46	50	4 1 7	70	-5	-15	50	59
5 2 1	-45	3	-25	-67	69	3 1 8	7	-21	-6	-20	19
7 4 1	34	-16	1	19	—	4 1 9	-4	1	15	12	—
2 5 1	-9	-13	28	6	—	9 1 10	-6	16	-4	8	—
4 5 1	45	17	2	64	70	5 1 10	-47	17	-4	-34	43
4 7 1	-21	-9	-9	-39	45	3 1 12	3	-17	7	-7	—
0 0 2	54	14	15	83	63						

The mean values of the distances Ce—Ce and Ce—O are 3.80 Å and 2.33 Å. These are very close to those found in CeO_2 : 3.83 Å and 2.32 Å, which shows that the cerium-oxygen bonds should be essentially the same in CeO_2 (6) and $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$. However, in the crystals of $\text{CeOSO}_4\text{H}_2\text{O}$ (2), the Ce—Ce distances within the chainlike $(\text{CeO})_n^{2n+}$ complexes are only 3.58 Å, whereas the Ce—O distances are in the normal range (2.4 Å). These short Ce—Ce distances, which are close to those found in cerium metal, suggest that the metal ion bonds in $\text{CeOSO}_4\text{H}_2\text{O}$ are different from those in $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ and CeO_2 . This is also supported by the fact that the compounds have different colours: $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{SO}_4)_6$ and CeO_2 whitish yellow and $\text{CeOSO}_4\text{H}_2\text{O}$ bright yellow.

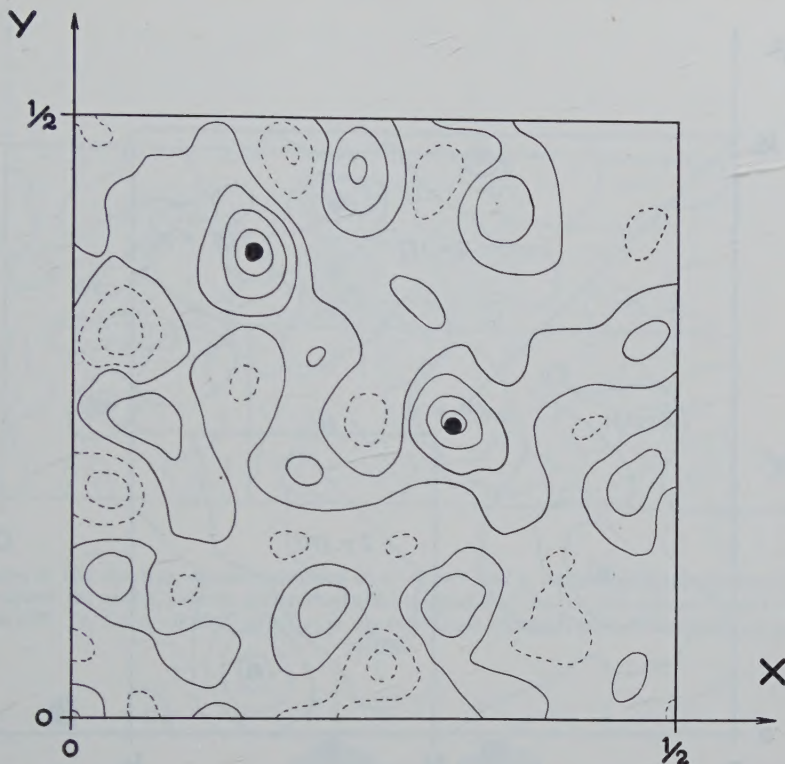


Fig. 6. Electron density section $q''(xy0)$ with the cerium (Ce_1 and Ce_2) and sulphur (S_1 and S_2) atoms subtracted. The positions of the oxygen atoms O_4 and O_5 are shown. Dashed lines indicate negative values.

The coordination of oxygen atoms around the cerium atoms is eightfold in all three crystals. In CeO_2 , they form a cube but, in $Ce_6O_4(OH)_4(SO_4)_6$ and $CeOSO_4H_2O$, they are arranged in the shape of a somewhat distorted square Archimedean antiprism.

The mean values of the S-O and O-O distances within the sulphate groups in $Ce_6O_4(OH)_4(SO_4)_6$ are 1.44 Å and 2.37 Å. This is in very good agreement with the distances given for sulphate groups in other compounds (a review is given by Wells (7)).

The distances between oxygen atoms in the $Ce_6O_4(OH)_4^{12+}$ complexes and the sulphate oxygen atoms are within the normal range showing that the lattice is also supported by O-O contacts.

Summary

The crystal structure of $Ce_6O_4(OH)_4(SO_4)_6$, isomorphous with $U_6O_4(OH)_4(SO_4)_6$, has been determined using Fourier methods. The calculations were in no respect based on the results published for the uranium compound. The deviations from the parameters obtained from the geometrically determined structure of $U_6O_4(OH)_4(SO_4)_6$ were then found to be very small.

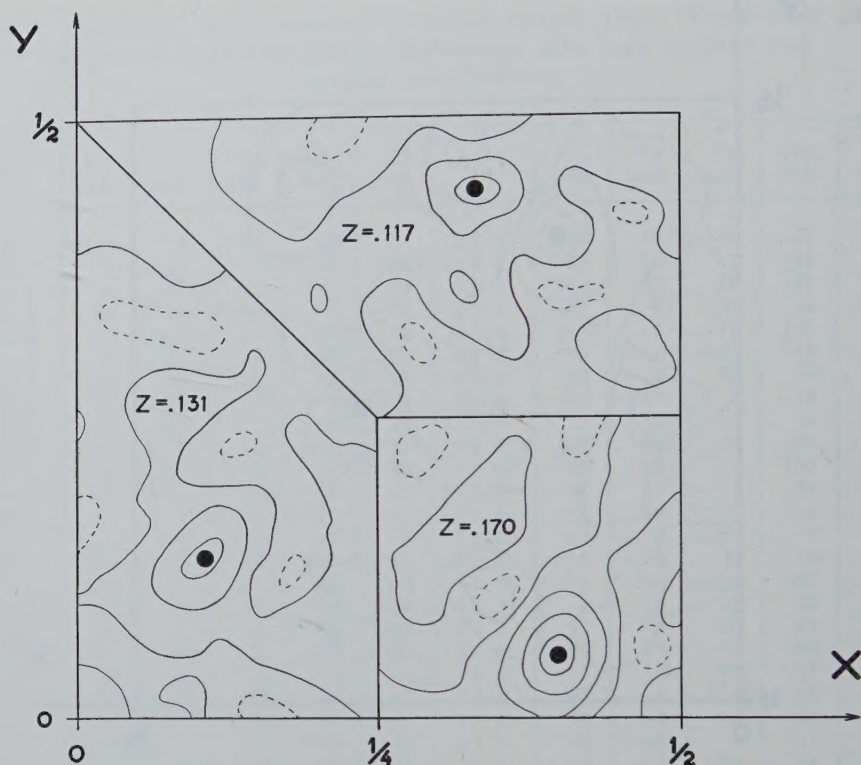


Fig. 7. Parts of the electron density sections at $z = 0.117$, $z = 0.131$ and $z = 0.170$ with the cerium (Ce_1 and Ce_2) and sulphur (S_1 and S_2) atoms subtracted. The positions of the oxygen atoms O_1 (in $z = 0.131$), O_2 (in $z = 0.170$) and O_3 (in $z = 0.117$) are shown. Dashed lines indicate negative values.

The structure is built up of finite complexes $\text{Ce}_6\text{O}_4(\text{OH})_4^{12+}$ held together by sulphate groups. The distances Ce–O, S–O and O–O (within the sulphate groups) were found to be close to those observed in other crystals. The Ce–Ce distances are the same as those in CeO_2 but definitely longer than those in $\text{CeOSO}_4\text{H}_2\text{O}$.

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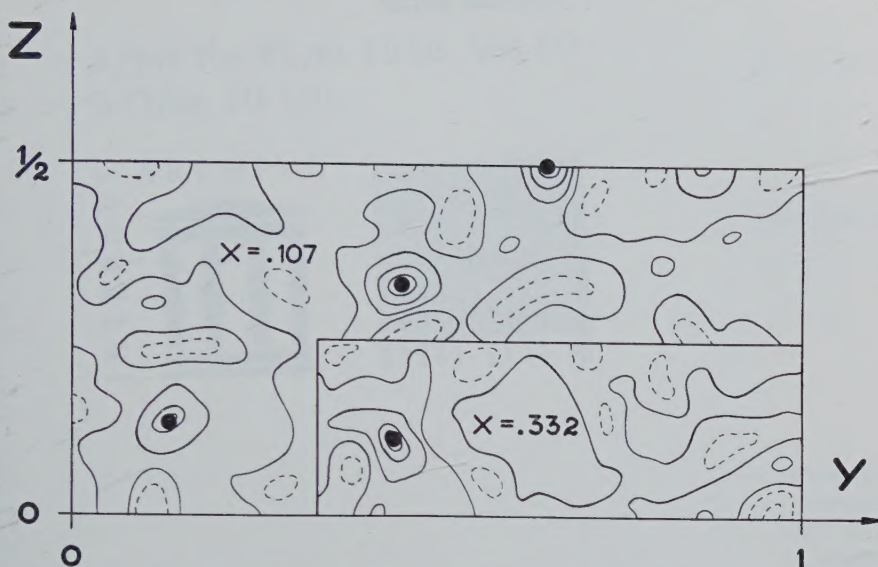


Fig. 8. Parts of the electron density sections at $x=0.107$ and $x=0.332$ with the cerium (Ce_1 and Ce_2) and sulphur (S_1 and S_2) atoms subtracted. The positions of the oxygen atoms O_1 (in $x=0.107$), O_2 (in $x=0.107$), O_3 (in $x=0.332$) and O_5 (in $x=0.107$) are shown. Dashed lines indicate negative values.

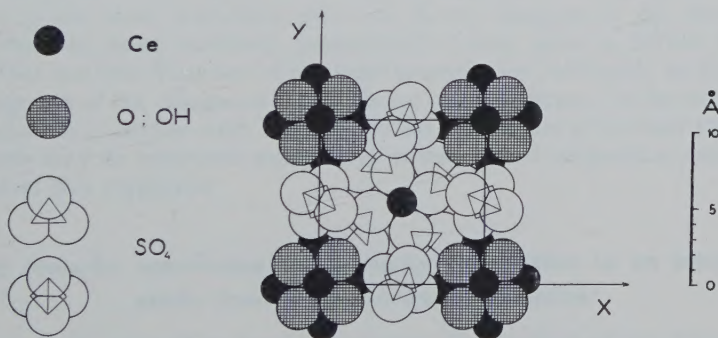


Fig. 9. Projection on the xy plane of a part of the structure of $Ce_6O_4(OH)_4(SO_4)_6$. (Only atoms with z parameters between 0 and $\frac{1}{2}$ have been indicated.)

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